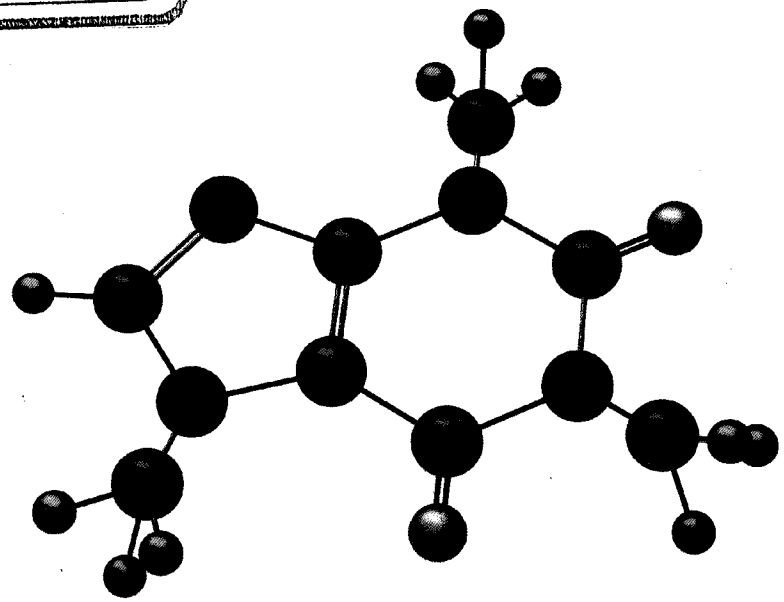

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# Interpolymer complexes

## Structure, properties, application

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**Mukhamedov G.I., Khafizov M.M., Inagamov S.Ya.**

# INTERPOLYMER COMPLEXES: STRUCTURE, PROPERTIES, APPLICATION

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Mukhamedov G.I., Khafizov M.M., Inagamov S.Ya.

**INTERPOLYMER COMPLEXES: STRUCTURE, PROPERTIES, APPLICATION**

The monograph gives a comparative evaluation of using interpolymer complexes in medicine, water economy and agriculture. Methods of preparation, physicochemical, mechanical properties and their structures are shown and the possibility of using interpolymer complexes as new materials for the formation of artificial blood vessels, biocompatible materials; thrombus resistance, as well as the relationship between the waterproof macrostructure and the functional properties that determine the productive capacity, corticity, soil erodibility; saving irrigation water. An original and promising way of using interpolymer complexes in medicine, water and agriculture for the rational use of water resources and protection of soils and the environment is proposed.

It can be used for chemists, physicists, pharmacists, physicians, soil scientists, meliorators, graduate students, researchers and students of higher educational institutions.

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Inagamov Sabitjan Yakubjanovich



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## FOREWORD

The authors of this monograph are fully aware that the time of writing large multivolume book on polymers, in particular on interpolymer complexes (IPC) has not come yet. At the same time, it seems quite feasible and necessary to give a picture of the ideas on which modern physics and polymer chemistry is based, without complicating this picture with unnecessary details. Of course, we also take into account that there are many good books and scientific articles devoted to individual and sometimes special problems. However, all these publications focus on the chemical properties of IPC. Accordingly, it seems necessary to systematize the field of application of interpolymer complexes in medicine, water economy and agriculture.

The authors sought to present in a compact form the main problems of the using interpolymer complexes and did not deal with the problems of creating IPC's, as well as polymer composite materials based on them, i.e., issues related to the using fillers, plasticizers, polymer mixtures, reinforced polymers, various polymer processing techniques, etc. Only the principal directions of the modification of the properties of the IPC are shown to improve the main technical indicators and increase the period of their operation

The range of known IPCs is very wide now. As polyanions, polymer carboxylate, sulfonate, and phosphate anions can be included in the IPC, polymer primary, secondary, tertiary and quaternary amines can be used as polymers. Components of IPC polyelectrolytes may have a synthetic origin, but may also be natural polymers, for example heparin and other polysaccharides.

Regardless of the specific chemical nature of the polyelectrolytes

forming the IPC, the reactions between them have a pronounced cooperative character. This is reflected in the fact that the destruction and formation of IPC occur in narrow intervals of pH change or concentration of salts.

The proposed monograph attempts to formulate the possibilities of practical using IPC in medicine, water economy and agriculture. The physicochemical properties of the IPC hydrogels open up wide possibilities for their application in various fields of medicine as semipermeable separating membranes, biocompatible coatings, dosing excretory systems, etc., and in water economy and agriculture as mulch material, hydrogels and anti-filtration screens to save irrigation water.



# INTRODUCTION

Studying multicomponent polymeric systems are constantly given great attention, as they are widely used to produce a variety of chemical fibers, artificial leathers, films and coatings, adhesives, varnishes and paints. At the same time, it should be pointed out that it is of considerable interest to clarify the physicochemical properties of multicomponent polymer systems. For they largely allow to solve a number of problems connected with physiological processes occurring in a living organism, and the technology of preparing artificial food products. Finally, such research and development is aimed at obtaining materials with predetermined properties.

The compatibility of polymers in plastics processing technology is important in obtaining a stable material from a mixture of two or more high molecular weight components. This is largely influenced by the conditions for mixing polymers. From the point of view of the physicochemical principles of the mixing process, the affinity of the polymers can be characterized by the solubility of the components (thermodynamic compatibility).

At the present time, a fairly extensive experimental material has been accumulated in the field of multicomponent polymer systems. In this connection, the works of Shwarz A.G. and Dinzburg B.N. [1], Karotenuto G. [2], Tager A.A. [3], Berlin A.A. and others [4], Kulezneva V.N. and Volfa V [5], Bekturova E.A. [6], Zezina A.B. and Kabanov V.A. are of the greatest interest [10-12].

The creation of a new class of highly effective materials that meets modern requirements of scientific and technical progress is becoming extremely important in connection with the possibility of solving a number

of important practical problems. Interpolymer complexes and composite materials represent a new class of composite materials with unique properties, due to which they find wide application in the national economy and thereby provide an improvement in the ecological situation. Due to the specificity of the structure of interpolymer complexes, it becomes possible to create on their basis polymeric materials possessing a wide range of properties, the production of which by other methods is not possible. The foregoing has determined the prospects for research in the field of interpolymer complexes and composite materials based on them, which have become the object of systematic research. Despite the many studies carried out in the field of interpolymer complexes, the problem of creating composite materials on their basis remains a very urgent task, caused by the need to solve key issues in the national economy.



# CHAPTER 1. INTERPOLYMER COMPLEXES

## 1.1. Methods of production and interaction mechanism of polymer-polymer complexes

The developing the theory of polymer-polymer interactions began with a systematic studying properties and structure of polyelectrolyte complexes A.S. Mikhaels with co-workers [7-9] (complexes of strong polyelectrolytes), V.A. Kabanov with co-workers [10-12] (complexes of weak polyelectrolytes) and Japanese researchers E. Tsushida with co-workers [13]. In this and other works, known from the literature, the interaction of weak polymeric acids and polycations (so-called "ionenes") carrying a charge in the main chain was studied mainly.

Obtaining polymer-polymer complexes is carried out by two fundamentally different methods:

1) interaction of chemically and structurally complementary macromolecules. Complementary, usually, are understood as such, macromolecules whose functional groups are capable of specific interactions, and the geometric structure of the macromolecules themselves does not prevent the formation of a sufficiently large number of intermolecular bonds, calculated on the polymer chain (i.e., mixing solutions of the finished polymer components) [14 ];

2) polymerizing the monomer on macromolecules - matrices previously introduced into the reaction medium (i.e. by matrix polyreaction, when the polycomplex is formed during the chain growth of one of the components on the macromolecules of the other) [15].

Of course, one should expect that a different mechanism of formation leads to complexes with different structure and properties. Indeed, in a number of works [10, 16], a difference was shown, both in the composition and in the properties of the complexes obtained by the above methods. Thus, for example, the comparison of complexes polymethacrylic acid (PMAA)-poly-N-dimethylaminoethyl methacrylate (PDMAEM) [10] obtained by mixing equimolar amounts of components and in the process of matrix polymerization of dimethylaminoethyl methacrylate in an aqueous medium, in the presence of PMAA, indicates that in the first case complexes are formed containing a half-fold excess of the acidic component are formed. At the same time, matrix complexes always form complexes containing matrix components, mainly in equimolar ratios.

The chemical nature of the arising bonds between heterogeneous macromolecules in polymer-polymer complexes can be different, namely, van der Waals, electrostatic, hydrophobic interactions, hydrogen and

coordination bonds.

By the type of dominant interaction, interpolymer complexes can be divided into several groups.

1) Complexes between polyacids of polyacrylic acid (PAA), PMAA and nonionic hydrophilic polymers - PVS, PEG, PVPD are characterized mainly by the presence of hydrogen bonds [17,18]. In [19, 20] using the example of a relatively simple PMAA-PVA system, certain features of the complexation process, accompanied by the appearance of intermolecular hydrogen bonds, were investigated.

In the first work on studying complexes with H-bonds (the work of F. Beyli with co-workers [21], K. Smith and co-workers [22]) it was shown that when water solutions of PAA and polyethylene glycol (PEG) are mixed, a water-insoluble complex of two polymers is formed. At the same time, data were obtained on the property (stiffness, glass transition temperature, viscosity) -component of a binary mixture of polymers. It was found that the curves of the dependence of viscosity on the composition pass through a maximum corresponding to 0.5% by weight of PEG. This result also indicates the equimolar composition of PAA-PEG complexes, which was later confirmed by other authors [23-25].

The formation of complexes in the studied systems occurs, in the opinion of the authors [21, 22], mainly due to the hydrogen bonds (-H ... O <) between the carboxyl groups of the polyacid and the etheric oxygen atoms.

1) A significant role of hydrophobic interactions in the processes of intermolecular association is noted in many works [24, 26-29]. This is shown, in particular, by the hardening the PMAA-PEG complex (MM = 2000) with increasing temperature [24]. A significant contribution of hydrophobic interactions in the formation of interpolymer complexes is confirmed by the thermodynamic characteristics of complexation.

It was experimentally established [26-29] that the formation of complexes in the aqueous medium is characterized by positive values of enthalpy and entropy (the reaction is endothermic). Several other enthalpy values are observed in PMAA-PEG systems [26] and PMAA-PVPD [29], which is due to the difference in hydrophobicity between PEG and PVPD. Viscosimetric data on the temperature stability of complexes in water and water-methanol mixtures correlate with the signs of thermodynamic parameters determined calorimetrically [24, 27]. It is further noted that the viscosity of complexes in water decreases with increasing temperature, that is, an increase in temperature facilitates the association of complementary macromolecules. This, apparently, is explained by the intensification of hydrophobic interactions due to a decrease in temperature. Stabilization of



[illegible] of complexes in these media is due to H-bonds, which are [illegible] enhanced with decreasing temperature.

If we consider the formation of complex polycomplex matrices + [illegible] polycomplex as equilibrium (or quasi-equilibrium), in which [illegible] is an independent particle, then the principles of equilibrium [illegible] can be used to describe such reactions [30].

For the simplest model of the complexation reaction, considered as the [illegible] of an oligomer on a one-dimensional lattice (matrix) [24], [illegible] are obtained that allow calculating thermodynamic parameters [illegible] as the change in the standard chemical complexation potential, the [illegible] of the reaction, and the half-life of the complex [15,26]. The [illegible] enthalpy of the complex formation of AN-500 cal /mole is in [illegible] agreement with the values of ΔH determined by calorimetric [illegible] ± 40 cal/mole) and potentiometric (320 ± 60 cal/mole) methods [15].

The cycle of works by V.A. Kabanov, I.M. Papisov and co-workers [illegible] refers to an in-depth studying the features of the formation of [illegible] matrix + oligomer <=> polycomplex and the fundamental [illegible] received products. From the combination of these and other [illegible] and theoretical data [38, 39], it was concluded that the [illegible] stage of matrix polyreaction is the recognition of its growth and [illegible] with the matrix through the cooperative interaction.

The stability of interpolymer complexes (polycomplexes) in solution [illegible] on the chemical structure of the components and on the chain [illegible] of the polymer partner with a lower degree of polymerization [27, [illegible]]. The introduction of a different hydrophobic group into the PEG [illegible] leads to a significant stabilization of its complex with PMC [illegible] polyacrylic acid in water [40]. In other words, it can be noted that the [illegible] of introducing a hydrophobic group into the PEM macromolecule is [illegible] to increase the length of the PEG chain.

1) The reactions of macromolecular substitution and displacement are [illegible] great interest [16, 41-48]. In these reactions, a high selectivity of the [illegible] between the polymers manifests itself in the fact that even weak [illegible] in the interaction energy lead to a difference in the strength of [illegible] polycomplexes formed by them. An example is the reaction: the [illegible] PEG + PVPD complex or the PMAA-PVA + PVPD complex. It [illegible] shown [16] that in aqueous solution the PVPD completely displaces [illegible] or PVA from their complexes with PMAA.

There are cases of substitution or displacement of one matrix (oligomer) from the polycomplex of another if the interaction of the latter with the complementary macromolecule is characterized by higher energy. In particular, the possibility of transition of an oligomer from one matrix to

another was demonstrated [45], using the PAC-PEG + PMAC complex as an example. And such substitution can go not only due to chemical nature and structure, but also depending on the length of the chain of the same oligomer. The formation of stable complexes in these systems is caused by the appearance of a multitude of interchain bonds, which is a consequence of the macromolecular nature of the reacting components.

In [15, 36], devoted to the cooperative interaction of synthetic oligomers with chemically complementary high-molecular matrices, an important conclusion was made about the nature of the distribution of oligomers over matrices under conditions when the oligomer was taken smaller relative to the matrices. By the example of PMAC reactions with the PEG oligomer, it is shown that in the case where the oligomer covers only a part of the matrices, a stoichiometric polycomplex is not formed. The rest of the matrix is in solution in a practically free state. Such a situation in the distribution of oligomers across matrices can be called "non-statistical", and this phenomenon is disproportionation.

A somewhat different approach in studying the interaction between high-molecular poly-N, N-dimethylaminoethyl methacrylate (PDMAEA) and oligomeric sodium phosphates (OpNa) was proposed in reseaches [49-51]. It is based on determining the number of chemical bonds formed by the links of the matrix with the oligomer units. In this case, it is not necessarily accurate to know the nature of the distribution of oligomer molecules in solution and on matrices.

Earlier, the ability of participation of water-soluble nonstoichiometric polyelectrolyte complexes (NPEC) in an interpolyelectrolyte substitution reaction has been thoroughly studied [52]:

$$\text{НПЭК (ПК}_1\text{ - ПК)} + \text{ПА}_2 \Leftrightarrow \text{НПЭК (ПА}_2\text{ - ПК)} + \text{ПА}_1 \qquad (1.1)$$

in which the polyanions PA1 and PA2 of different chemical nature compete for binding to the PC polycation. Studying similar model reactions allowed the author to reveal the general kinetic and thermodynamic factors responsible for the restructuring and rearrangement of biologically significant macromolecular structures. It was further established [53-55] that the equilibrium position of reaction (1.1) can be controlled by varying the concentration and nature of the added low molecular weight salts, as well as the degree of polymerization of polyions and temperature [56].

4) At present, polyelectrolyte complexes formed due to reactions between macromolecular acids and bases (or their salts), which are stabilized by salt bonds, have been studied in sufficient detail.

Analysis of the large experimental and theoretical material available in the literature [7,8,11,12,14,57-60] indicates that the main regularities of the



formation of polyelectrolytes were obtained in the study of the equilibrium state of phases in coacervate systems. At the same time, the scientific and theoretical approaches to the investigation of the polymer-polymeric salt were the same as for more real three- and four-component systems.

Based on the literature data on intermolecular interaction in the formation of a homogeneous system, i.e. in conditions of compatibility of mixing polymers, the following will be observed:

$$E_{11}=E_{12}=E_{22} \qquad (1.2)$$

where: $E_{11}$, $E_{12}$, $E_{22}$ - the energy of pair interactions of the same and dissimilar macromolecules.

Parameters of thermodynamic interaction can be estimated using the experimental method of determining free energy. It is based on obtaining isotherms of individual components and their mixtures using a common solvent for two polymer blends [61].

To clarify the mechanism of complex formation between weak polymeric acids (bases) and salts of polymer bases (acids), Zezin A.B. with co workers [10, 12, 62-65] recommended a method for calculating the degree of conversion of Q from potentiometric titration curves, which is depicted as follows:

$$Q=C_к/C_0 \qquad (1.3)$$

where, $C_к$ is the concentration of salt bonds, base-mole/l; C is the initial concentration of polyelectrolyte, basic mole/l.

To assess the nature of the interaction between two polymer components in a common solvent, a viscometric method was used [66]. The influence of the solvent on complex formation was also studied [67].

A number of papers [14, 68] are devoted to studying the interaction of homogenic polypeptides with synthetic polyelectrolytes. It is shown that the polycomplexes can stabilize both disordered (coil-like) and ordered (a-helix) conformation of polypeptides. In addition, in a number of works [12,14,68,69-71], a significant role of the steric matching polyelectrolytes in interactions with each other was established.

There are enough papers in the literature describing the results of the successful application of physicochemical methods for complexation reactions. Thus, the reaction of formation and destruction of a polyelectrolyte complex (PEC) was studied by the potentiometric titration method [72]. It is shown that in these reactions the amount of salt bonds Q stabilizing the PEC depends on the pH of the solution. In a weakly acidic medium, where the proportion of salt bonds in the complex is Q<0.6, PEC exists in the soluble state. Finally, in a neutral and slightly alkaline medium, the reaction of complexation tends to completion, the amount of salt bonds in the complex is increased (Q->1). As a result of all this,

hydrophobization and loss of solubility in water are observed.

PEC as hydrophilic polymeric compounds are used for the production of semipermeable membranes [73-75], coatings [76], effective flocculants [77], structurants of disperse systems [78,79], as well as for various medical purposes [80,81]. There are also works devoted to the further improvement of the physic-chemical properties of PEC [82, 83] for even greater practical use.

For a series of PEC containing a weak polyelectrolyte as one of the components, a pH interval was found in which these PECs will be resistant to dissociation into the original polyelectrolyte components. And this, in turn, largely depends on the degree of polymerization of the latter [13, 50, 51, 84]. In such systems, the equilibrium of the PEC formation reaction can be shifted by the pH of the medium, leading to a change in the charge of the weak polyelectrolyte.

Disbalances in the equilibrium of the PEC formation reaction can also be achieved by varying the concentration of low molecular weight salt in the system [85-88]. It was demonstrated in [88] that the stability of PEC with respect to dissociation into its constituent polyions in aqueous-salt solutions strongly depends on the chemical nature of the low-molecular electrolyte. And in [70] a systematic study was made of the effect of the degree of polymerization of polyions on the stability of PEC in aqueous-salt media.

5) Intermolecular reactions of such systems are of particular interest in that they are usually polyfunctional and complexes based on them are stabilized by two or more types of bonds. Investigation of interpolymer reactions in more complex, for example, multifunctional macromolecular systems makes it possible to purposefully change and carry out the interaction reaction between polyfunctional compounds.

Literary data on complex formation involving biopolymers with synthetic high-molecular compounds and synthetic polypeptides are considered in detail in the works of G.V. Samsonov and co-workers. [89-92]. They give answers to questions of the formation of protein-polymer complexes, as well as the mechanism of their interaction.

The polycomplex, one of the components of which is chitosan (ChTS), is of the greatest interest from biopolymer-based PEC [93,94]. They have ecological purity and unique properties, which is why they are widely used in medicine, pharmacology and in a number of other areas [95]. It should be pointed out that the prepared medical materials of PET ChTS with the known anticoagulant blood - heparin [96,97] and other anion-exchange polysaccharides such as sodium dextran sulfate [98-100], carboxymethyldextran [101,102] and carboxymethylcellulose [94,103]



have antithrombogenic properties.

It was very interesting to conduct studying in the field of complexation of metals with macromolecular ligands [104 ± 107]. In particular, coordination complexes of acceptor polymers from nitropthalic acids with donor macromolecules based on arylimino diethanol [108-112], complexes of copper b-diketonates and polyoxyethylene glycols [113,114], as well as ternary polymer-metal complexes such as polyacrylic acid-$Cu^{2+}$ - polyethylenimine [ 115,118], polyacrylic acid-$Cu^{2+}$ -poly-4-vinylpyridine [119,120].

There are complexes of a mixed type, stabilized by two or more types of connection [121,122]. As a rule, besides the main type of bonds, interpolymer complexes can be stabilized additionally by other interactions, for example, hydrophobic ones.

The complexation of carboxymethylcellulose (CMC) with polyamines under various reaction conditions is described in greater detail in [123-125]. It is indicated that many of their properties depend on the pH of the medium and the reaction conditions. In addition, the thermodynamic phenomena of complex coocervation in phase separation are investigated.

The complexation reaction of CMC with a linear polyelectrolyte having positively charged dye and starch ions was considered in works [126, 127]. It is shown that the complexes are stabilized due to salt hydrophobic and hydrogen bonds.

Of particular interest are the results of an investigation of the CMC complex with synthetic polymers in solution [128, 129]. The authors note that polyethyleneimine (PEI) binds to anionic cellulose derivatives not only with salt bonds, but also with H bonds that arise between the amino groups of PEI and free hydroxyl groups of cellulose. Desorption curves of the CMC-PEI complexes are given in the work [129]. It is noted that under certain conditions, chains of different nature with different distances between ionic groups and different dissociation constants give stoichiometric complexes.

The physicochemical properties of various complexes of the polycation-polyanion type were investigated depending on the ratio of reagents and the pH of the medium [130-132]. Data are also given on the morphological structure of complexes obtained by optical and electron microscopy [130]. In addition, the reaction between polyelectrolytes CMC and various polycations [131,133], both formation and their destruction, has been studied by potentiometric titration [132].

CMC with different polycations forms interpolymer complexes stabilized by salt and hydrogen bonds [122,133,134]. They certainly possess a whole complex of valuable properties [135], including high

biocompatibility, non-toxicity [136]. They are easily prepared from aqueous solutions. They represent a sufficiently high chemical and thermal stability.

Thus, in the studies discussed above on the synthesis and study of interpolymer complexes, special attention was paid to the nature of interactions between chemically complementary groups in interpolymer and polymer-oligomeric complexes. It should be noted that at the present time the features of the interaction of biopolymers with synthetic polypeptides, their thermodynamic parameters and the areas of their application can be fully represented. In this connection, it is worth noting the works of G.V. Samsonov [89.90], A.B. Zezin [12,14,57], E. Tsushchida [58,59,118,137], N.A. Plate, V.A. Kabanov, E.A. Bekturov [32,138,139] and others [140].

At the same time, it should be pointed out that polycomplexes based on polyfunctional polyelectrolytes of non-stoichiometric composition have been studied to a much lesser degree. The use of such polyelectrolytes, it seems to us, makes it possible to vary physic-chemical properties of the complexes formed within rather wide limits. It must also be assumed that the results of such studies ultimately lead to the production of not only new IPCs, but also allow predetermining the structural and chemical characteristics of such materials.

### 1.2. Stoichiometric, nonstoichiometric complexes and composites

IPCs are products of interaction of chemically complementary macromolecules - polyanions and polycations or donors and proton acceptors. Unlike ordinary chemical reactions between low-molecular substances, the interaction between macromolecules is of a cooperative nature. The emergence of a link between the links of complementary chains, the strength of which coincides with the strength of the corresponding bond between small molecules, greatly facilitates the formation of subsequent interpolymer contacts. This provides an exceptionally high stability of the IPC even if the free energy of formation of a single bond is not high [14]. So, unlike simple salts, almost completely dissociated in aqueous solutions, the polymer-polymer salts formed by the interaction of oppositely charged polyelectrolytes and called interpolyelectrolyte complexes (IPEC) are fully associated.

IPC is divided into two groups - stoichiometric interpolymer complexes (SIPCs), in which chemically complementary units are included in an equimolar (1:1) ratio, and nonstoichiometric interpolymer complexes



(NIPC's) containing an excess of one of the components. Figure 1.1 shows a schematic representation of the structure of SIPC and NIPC.

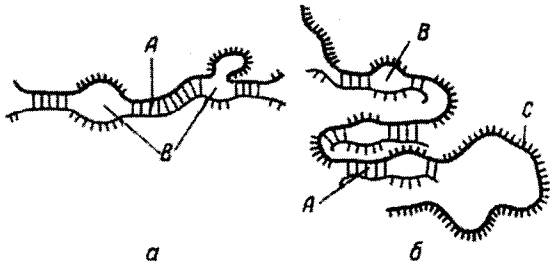



*Fig.1.1. Structure of SIPC (a) and NIPC (b). (Explanation in the text).*

Two types of alternating sections can be distinguished in the structure of the IPC: more or less extended two-stringed sequences of pairs of links of heterogeneous chains that formed links with each other (section A) and loops, including disconnected links (section B). The difference between SIPC and NIPC is that the latter, along with these sections, contain single-stranded sequences of polymer units included in the NIPC in excess (section C). It is these single-stringed chain parts that ensure the ability of the NIPC to dissolve in contrast to the SIPC.

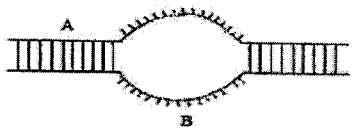
It is interesting to note that along with the high stability of IPC with respect to dissociation in these compounds, shown schematically in Fig.1.1, it is quite easy - at high speeds, some interpolymer contacts are replaced by others, while their total number remains unchanged, i.e. the chains that make up the IPC particle are able to move relative to each other like caterpillars. In this case, macromolecules can even migrate from one IPC particle to another, exchanging or replacing one another. Such processes, accompanied by transferring polyions and known as substitution and exchange reactions, have been studied most extensively with respect to IPEC [52,87]. The rate of migration and transfer of polyions and the direction of these processes can vary within very wide limits, changing the degree of hydration of IPEC, as well as the pH and concentration of simple salts in the environment. Thus, in the absence of low molecular weight electrolytes, such reactions practically do not occur, and when small amounts of salts, for example, 0.1 M NaCl, are added, ends within a fraction of a second [70,85,88,141].

The literature presents the results of the interaction between poly-electrolytes [12,14,15,90,141], containing components in equimolar ratios. It can be pointed out that at present the main attention of researchers in the

field of polyelectrolyte complexes is turned to effective methods for their production. Somewhat less attention is paid to the studying the structure and properties of polyelectrolyte complexes of non-stoichiometric composition. And this, it seems to us, does not allow us to more fully and reliably predict the properties of the materials obtained.

Note that for the first time a new type of water-soluble protein-polyelectrolyte complexes was obtained by Samsonov G.V. [89], who carefully studied the interaction of bovine serum albumin (BSA) and poly-N-ethyl-4-vinylpyridine. It turned out that the globules of protein included in the complex in excess, play the role of a lyophilizing component and ensure the solubility of the complex.

Such complexes are characterized by staircases [50,86]. It should be pointed out that they are characterized by more or less ordered sections, which are double-stranded sequences of pairs of oppositely charged links. It was found that the salt bonds (A) alternate with the regions (B), containing disconnected links and representing loops-like defects. A fragment of such a structure is depicted on the diagram:




(1.4)

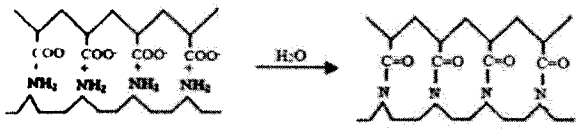
These features of the structure and properties of the IPC open wide opportunities for their use in various areas of practical activity, including in medicine, agriculture, and water management. IPC particles have colloidal properties similar to protein structures, the most characteristic of which are charge, hydrogel structure, controlled permeability in water and solutions containing components of physiological fluids [142]. A consequence of this is the unusually good biocompatibility and hemocompatibility of IPC.

### 1.3. Chemical reactions of synthesis of interpolymer complexes

Let us now consider some reactions of the formation of interpolymer complexes according to the classification proposed above. Such reactions can occur between polyelectrolytes in solutions or in bulk. Some of them lead to the formation of ionic or hydrogen bonds between the links of macromolecules, some to the formation of hydrophobic and coordination bonds. Such transverse bonds can form between each of the links of macromolecules that are capable of chemical interaction with a link of another chemical nature, which will lead to the formation of macromolecular structures of the ladder type. An example is the reaction of

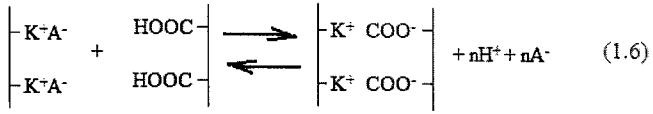


polyacrylic acid with polyethyleneimine in the form of their polyelectrolyte complexes [14]:




(1.5)

The essential characteristic of polyelectrolytes in reactions with each other is the strength of the base and the strength of the acid. When mixing aqueous solutions of salts of poly-bases with a polyacid, decreasing in the pH of the mixture is observed [11]. Such behavior of a mixture of two polyelectrolytes can be explained by the reaction between polyelectrolytes with the release of protons and the formation of a salt polyelectrolyte complex according to the scheme:

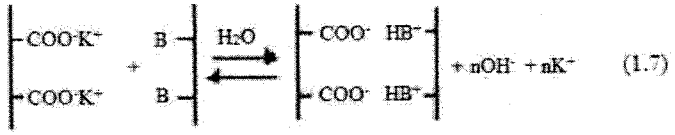


(1.6)

The equilibrium of a similar reaction for low-molecular model compounds is almost completely shifted to the left. Moreover, the reaction does not occur even if only one of the components is of a polymeric nature.

One of the products of reaction (1.6) is a polyelectrolyte complex, insoluble in water. This is due to the hydrophobization of macromolecules, since the ionogenic groups responsible for the solubility of polymers in aqueous solutions turn out to be blocked. If such solutions are titrated with alkalis, then one can observe an increase in opalescence due to the further course of the formation of the polyelectrolyte complex. The complex is isolated from the solution in the form of particles having a globular structure, which can be judged on the basis of electron microscopic studies [12].

In addition to the reactions just considered, unconditional interest is represented by exchange reactions between the same pairs of polyelectrolytes that occur in alkaline media. In such solutions, the polymeric acids are practically completely ionized, and the macromolecules of the poly-bases are uncharged. In this case, the reaction between polyelectrolytes can be represented by the scheme:

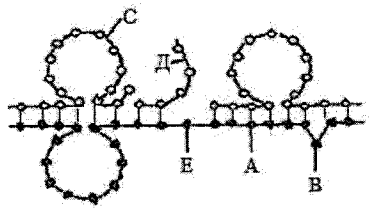


(1.7)

According to the scheme (1.7), the reactions between salts of weak polyacids and weak poly-bases should be accompanied by an increase in the pH of the solution and the formation of a salt complex. The equilibrium of the reaction (1.7) can be shifted towards the formation of a polyelectrolyte complex by introducing into the acid solutions, for example, HC1.

Using matrix polymerization to produce a polycomplex with the aim of converting them into ladder polymers appears to be very promising considering the variety of structures of the precursors (i.e. polycomplexes) that can be synthesized in this way.

The possibility of the formation of perfect double-strand structures is particularly important in the chemical modification of polycomplexes. The reactivity of the monomeric units of the macromolecular components of the polycomplexes in each given reaction depends on which of the structural elements these units belong to: double-stranded sections A or defects in the structure of type B, C, D or E (Scheme 1.8):



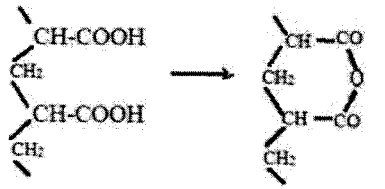

(1.8)

Therefore, each given reaction can take place in different structural elements of the complex at different rates up to a given spatial separation of certain reactions.

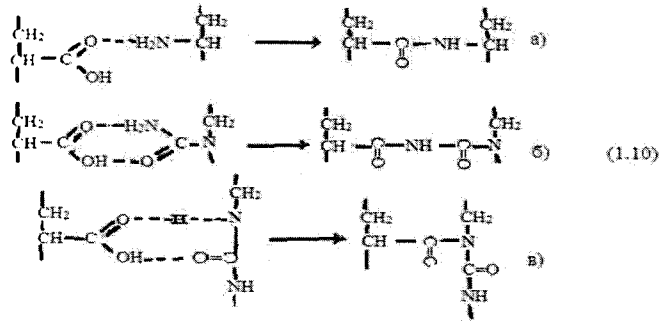
Intramolecular cyclization in polycarboxylic acids bound in a polycomplex (Scheme 1.9) occurs only in loops. It is indicative that the proportion of loops in the matrix polycomplex after its dissociation into macromolecular components and subsequent reconstruction (this was achieved by alkalizing the solutions of the polycomplex to pH 8, followed by acidification to pH 2.5) was exactly equal to the lobe ratio in the polycomplex obtained by mixing the polymers [15,23]: In contrast, intermolecular reactions with the formation of covalent bonds between polycomplex chains occur only in double-stranded regions, for example,



imidation reactions in polycarboxylic acid complexes with sex iamines [10, 11, 14] (Scheme 1.10a), imidation reactions in complexes of the same polyacids with polymers containing primary or secondary amide groups [141,148,149] (schemes 1.10 b and 1.10 c):



(1.9)



(1.10)

The products of such intermolecular reactions are polymers of the ladder structure. The more perfect the double-strand structure of the initial polycomplex, the more perfect the ladder structure the polymer can be obtained.

Polymer-polymer complexes stabilized by H bonds are formed by the interaction of structurally and chemically complementary macromolecules containing groups capable of forming them. These are complexes of weak polymeric acids (polyacrylic, polymethacrylic) with nonionic hydrophilic polymers - polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyvinylpyrrolidone (PVPD), polyacrylamide (PAA).

An insoluble precipitate is formed when mixing concentrated aqueous solutions of PAA (PMAC) with PVPD, PAA and PEG [110, 139, 140]. Spectral studies of PAA, PVPD, and the PAC-PVPD association product indicate the formation of a system of H-bonds between PVDD and COOH carbonyls by polyacid groups [18].

The structure of the associate formed in a complex manner depends on many factors, and primarily on the prehistory of the solutions - their initial concentrations, pH, and aging time. The most ordered form are fibrillar structures. The formation of stable complexes in these systems is due to the appearance of a multitude of interchain contacts, which is a consequence of the macromolecular nature of the reacting components.

Thus, the reactions of formation of interpolymer complexes have a distinct cooperative character, which is due to the large number of interacting groups located at corresponding distances in two interacting molecular chains.

Interest in the studying such products of the association is due to the possibility of their use in engineering, water economy, agriculture and medicine, as well as to create various functional macromolecular systems, such as, for example, ternary polymer-metal complexes and nanocomposites or self-regulating enzyme systems.

The considered reactions are of great importance, since they show that the formation of complexes characteristic for the specific interaction of polymers (for example, the formation of enzyme-substrate complexes, antigen-antibody) is not always limited to macromolecules arising in living organisms.



# CHAPTER II. PHYSICO-MECHANICAL, CHEMICAL PROPERTIES OF INTERPOLIMER COMPLEXES AND COMPOSITES

## 2.1. Features of complementary macromolecules interaction

As noted above, polycomplexes are usually prepared by mixing the finished polymer components in a common solvent [7,10,11,12,14]. They are characterized by a certain composition, and the physical and chemical properties of polycomplexes differ significantly from those of the original polymers. Cooperative systems of intermolecular bonds cause high stability of polycomplexes even in dilute solutions, although under certain conditions (temperature, reaction medium) they can be partially or completely destroyed. A more detailed description of polycomplexes can be obtained from the published papers [7,9,12,32,90,139,143].

Practically any interpolymer complex (IPC), formed when mixing the finished polymer components, can be obtained by matrix polymerization. As a method of IPC synthesis, matrix polymerization is characterized by a number of advantages, namely: a reduction in the number of stages of synthesis; the possibility of synthesizing more ordered double-strand structures; the possibility of varying the structure of the daughter polymer and, consequently, the structure and properties of the IPC by varying the conditions for the synthesis; the ability to synthesize such IPC and composites that are difficult or impossible to obtain by mixing finished polymers; the possibility of changing the structural organization of the polymer at the stage of its synthesis by introducing into the reaction system very small amounts of the matrix.

When polymerizing polyfunctional monomers, cross-linked insoluble products are often formed. Matrix polymerization of such monomers or the preparation of soluble oligomers therefrom is the most practical way of obtaining IPC.

For example, such a cheap polymer **as urea-formaldehyde resin** (UFR) is very attractive for use as components of IPC. It is usually insoluble, so the only way to incorporate it into the IPC is matrix condensation polymerization of the starting monomer, or soluble oligomer on specially selected macromolecular matrices.

IPC of UFR and **polyacrylic acid** (PAA), 1:1 composition (based on monomer units), were obtained for the first time by matrix polymerization of urea and formaldehyde on PAA in aqueous solution [33,144-146].

Below, details of the interaction of UFR with **carboxymethylcellulose** (CMC), as well as some properties of the obtained IPC, will be discussed in detail.

Figure 2.1 shows the scheme of matrix polycondensation of urea and formaldehyde in the presence of CMC. In the initial solution of the matrix (a), first, a gel is formed, which is a composite swollen in water. It consists of the UFR-CMC IPC formed during the matrix reaction and the CMC excess, Fig. 2.1 (b). Over time, the composite is enriched with IPC and when the free matrix is exhausted, only the IPC swollen rice remains in the reaction system 2.1(c). Because of further polycondensation, a composite is formed, consisting mainly of IPC and UFR in Fig. 2.1 (d).

The composition of the final product of the matrix reaction depends on the stage at which the process is stopped, i.e. from the initial ratio of the matrix to the UFR in the reaction system. Here it should be noted that the structure of the chains of UFR, and consequently the structure of the IPC, depends on the pH of the reaction medium. So, by varying the composition of the reaction medium and the initial ratio of UFR and matrix, it is possible to obtain a variety of composite materials from the same polymers by matrix polymerization.

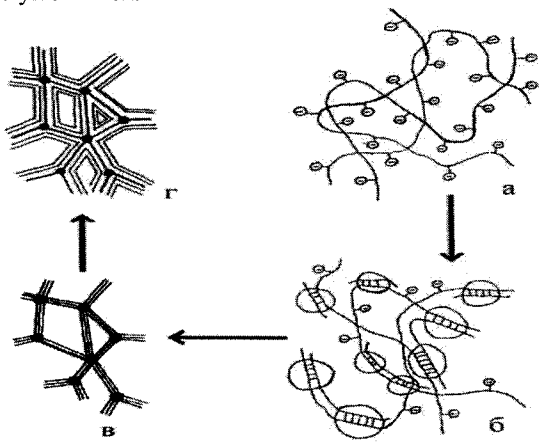



*Fig. 2.1. Scheme of product formation during matrix polycondensation of urea and formaldehyde in the presence of CMC: a-moderately concentrated matrix solution; b-gelation (composite including IPC and excess CMC matrix); in-stoichiometric IPC UFR-CMC; g-composite, including IPC and excess UFR.*

Composites consisting of IPC UFR-CMC and excess matrix-CMC, are hydrogels capable of absorbing from 800 to 1000 volumes of water per one volume of dry composite.



The authors of this monograph have shown that the resulting IPC CMC-UFR systems are very stable in neutral and slightly alkaline media due to the rather strong ionic bonds between the components that make up them. It is further ascertained that, as the acidity of the medium decreases, the number of interpolymer bonds stabilizing the IPC increases. The latter is also due to the appearance of additional hydrogen bonds.

It is known [12,15,32] that in interpolymer systems even ideally complementary, more than 20% of defective sites are formed in which the links of dissimilar macromolecules are disunited. If we take into account that the CMC-rigid macromolecule and the density of its charges are much higher than in UFR, then under the conditions of carrying out the experiment with complex formation, the formation of defect sites is inevitable.

The resulting structure of the complex macromolecule of water-soluble IPC can be considered as a sequence of bound sufficiently extended hydrophobic and hydrophilic blocks.

Further, we point out that the structure of interpolymer complexes of CMC-UFR can be varied by changing the ratio of CMC and UFR, and thus obtain products with a wide range of physicochemical and mechanical properties. We have obtained a variety of IPC CMC-UFR samples, which are further carefully investigated by complex methods. They were also subjected to various tests to assess their performance.

The results of studying the mechanical strength at rupture of IPC films show the complex character of the change in the value of the strength *s* with the change in the ratio of the interacting components (Fig. 2.2). The initial addition of CMC to the composition of UFR leads to an increase in the mechanical strength of the films. With an equimolar composition of interacting components, the maximum value of mechanical strength is observed. A further increase in the CMC content in the films leads to a certain decrease in the mechanical strength. This can be explained as follows. Naturally, one must assume that there is an excessive amount of CMC in the IPC and the prepared films have a heterogeneous supramolecular structure. Obviously, the particles of the polycomplex (PC) form one region, and the chemically unrelated macromolecules of the CMC are the second. This is quite possible, since the CMC macromolecules under the conditions of obtaining IPC (pH=2:3) are in a state of statistical coil [122,133]. Thus, two regions are observed in the sample, the first of them is saturated with PC particles, the second - with an excessive number of CMC balls [122].

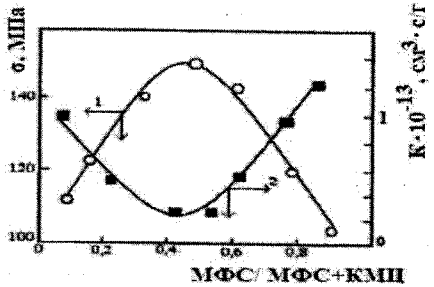



*Fig. 2.2. Dependence of mechanical strength (1) IPC with a rupture in the air-dry state and a change in the coefficient of water permeability (2) IPC films from the ratio of components. Temperature 298 K.*

Of course, an increase in the share of UFR also leads to the emergence of a heterogeneous structure consisting of IPC and excess UFR. The matrix CMC controls the polycondensation of UFR, so the excess of the latter does not form an independent condensate product. The formed UFR differs from the UFR obtained without CMC, as evidenced by the data given in [133]. As a result of all the marked, it should be concluded that the mechanical stress is also distributed non-uniformly. And this, naturally, leads to a decrease in mechanical strength (Fig.2.2).

Figure 2.2 shows the dependence of the water permeability coefficient "K" of IPC films and their composites on the basis of CMC and UFR at constant pressure P = 0.2 kg/cm². Water permeability was studied by the rate of water flow through the film, according to a known technique [14].

As can be seen, the "K" films with an increase in the UFR content to an equimolar composition decrease, and further growth of the UFR causes an increase in the permeability coefficient. It was ascertained earlier [12] that the water permeability of interpolymer films depends on the hydrophilicity, the packing density of macromolecules and on the number of transverse bonds. Consequently, the minimum value of K observed when the equimolar composition of CMC and UFR is related to the formation of the greatest number of intermolecular bonds between the reacting components and the dense packing of the formed globular IPC particles. An increase in the permeability coefficient of films with an excess of one or the other component will be due to the process of loosening and the formation of a heterogeneous (porous) structure. This is due, in particular, to the presence of excess hydrophilic functional groups of CMC (-COO) and UFR ($NH^+$, $NH_2^+$) in the system.

When mixing CMC and UFR, obviously, there is an interaction



between carboxyl groups of CMCs, as well as amide groups of UFR. This is clearly indicated by the shift of the absorption bands at 1400.16 010 to 20 40 $cm^{-1}$ in the low-frequency region in the IR spectrum and PC, which was synthesized in an acidic medium (pH =2/3).

The change in the structure of the CMC materials formed with urea-formaldehyde resins naturally leads to the production of new IPCs with specific properties and structure. Thus, in the IR spectrum of the IPC of CMC-UFR, the intensity of the absorption bands of carboxylatanion (vCOO) at 1550 $cm^{-1}$ (amide-II), 1650 $cm^{-1}$ (amide-1) is increased and broadened due to the presence of these groups in the interpolymer connection. Along with this, the intensity of the absorption bands of the deformation vibration of the carboxylatanation (vCOO$^-$) at 1420 $cm^{-1}$ is also observed (Fig. 2.3). These data undoubtedly help to identify the samples of IPC that we have obtained in different composition and structure.

In the IR spectrum of the interpolymer complex CMC-UFR (Fig. 2.3, c.), significant changes in the position of the maxima of the absorption bands, their intensity and width are observed in comparison with the UFR spectrum. It is easy to establish changes in the position and intensity of the bands in the IPC spectrum in the 1730 and 1610-1680 $cm^{-1}$ region. Since the deformation vibrations of NH groups contribute to the absorption in this region, these changes indicate the involvement of these groups in the interaction between the components of the polymer complex. This is also evidenced by the general broadening of the band in the 3500-3200 $cm^{-1}$ region [147].

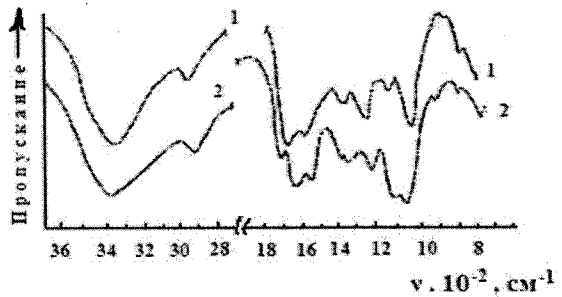



*Fig. 2.3 IR spectra of UFR (1) and interpolymer complex CMC-UFR equimolar composition (2), obtained at pH = 2.5-3. Temperature 298 K.*

Based on the IR spectroscopic studies, it can be concluded that the IPC of CMCs with UFR of different structures are stabilized both by ionic

bonds between the carboxylatanions of CMC and the amino groups of UFR and by the hydrogen bonds of the carboxyl groups of CMC with the carbonyl groups of UFR, which, in turn, confirms the previously expressed conclusions [122,147].

Our research, at the same time, indicates a certain difference in the mechanism of IPC formation. To confirm this statement, we can give the following example. Thus, a polycomplex (PAA and UFR) was obtained as a method of matrix condensation of urea and formaldehyde in the presence of the macromolecule of PAA [144-146,148,149], and by mixing PAA with cyclophage UFR at pH 3-4 [150].

The polycomplexes obtained in both cases, as indicated by the authors of the works, are stabilized by hydrogen bonds, which form practically unlimited sequences of intermolecular bonds with the same intramolecular mobility of complementary chains in the polycomplex. The co-operative nature of the systems of oligomers associated with the matrix can be the conformational transformation of the matrix when complexed with oligomers [32, 148].

Studies have shown that the IPC CMC-UFR, in contrast to the PAA-UFR polycomplex, is stabilized not only by hydrogen but also by ionic bonds, the relationship between which depends on the acidity of the solution. Thus, at pH = 2/3 hydrogen bonds predominate, and at pH = 7- ionic. In an acidic environment, the excess of the CMC or UFR excess with respect to the equimolar quantity leads to an increase in the density of the hydrogen bonds. In this case, even the existence of two types of hydrogen bonds is possible: between the links of chemically complementary chains of CMC and UFR (denoted by OH ... N) and between links of the same chain (OH ... O). Presumably, the latter can belong to either the same or different IPC particles.

Thus, it follows from the obtained results of the investigation that when the pH of the medium and the ratio of constituent components to the IPC change, deep structural transformations occur due to ionic and hydrogen bonds. Due to the latter it is not only possible to obtain IPC, but it is also possible to control properties such as water permeability, porosity and deformation-strength properties in aqueous media. And this, in turn, allows the process to be carried out purposefully and to receive materials (for example, IPC films) with prescribed properties for medicine, agriculture and water management.



## 2.2. Complexation of carboxymethyl cellulose with different polycations

Note that studies of interpolymer reactions between polymers of natural origin and synthetic physiologically active ionogenic oligomers, as well as a comprehensive study of the structure and properties of IPCs, including dependence on the nature and structure of the initial components, is one of the topical problems in the chemistry of high molecular compounds. As a result, in particular, it will be possible not only to receive environmentally friendly products, but also to reveal a number of scientific and practical problems in the field of synthesis and application of interpolymer complexes.

Below, we will present the main results on the synthesis and physicochemical studies performed on the basis of CMC with nitrogen-containing polymers-UFR, PMAG, PHMG and natural silk sericin. These studies are, as it were, a continuation of the solution, mainly, of such a task as the production of new environmentally friendly polymer products with specified properties and the identification of the main regularities in predicting the structure and properties of the products obtained. It should be assumed that such an approach in the choice of polycations will make it possible to establish some characteristic features of the CMC complexation process, not only in connection with the charge density in the oligomer chain, but also the polycation structure.

Complexation is accompanied by a change in the concentration of hydrogen ions in the solution. This allows us to use the methods of potentiometric, turbidimetric and viscometric titration to study the possibility of complexation in various systems of interacting complementary macromolecules.

Figures 2.4-2.7 show typical curves of potentiometric, conductometric and viscometric titration using the example of the **carboxymethylcellulose-urea-formaldehyde resin** system (oligomer), **polymethyleneamino guanidine, polyhexamethylenguanidine** (CMC-UFR, PMAG, PHMG). The inflection point on the titration curves indicates the composition of the interpolymer complexes in the system under study. The characteristics of the polymers used are given in Chapter 4.

Figure 2.4 shows that the pH increase for mixtures of CMC and UFR is small (ΔpH = 0.2-0.5), which indicates a weak intermolecular interaction of constituent components. The optimum composition of the reaction mixture CMC:UFR indicates a diffuse maximum of the stoichiometric composition. The blurring of the maximum is obviously due to the presence in the polycation of various amino groups (tertiary, secondary) with a low charge density.

The results of studies of the interpolymer reaction of CMC-PMAG and CMC-PHMG clearly indicate that the initial components enter the complex in nonequimolar ratios. In Figures 2.4-2.7 it is easy to see that the pH dependence of the composition passes through the maxima corresponding to the characteristic compositions of the IPCs formed. Such a composition seems to be very characteristic for the CMC-UFR system, z = 0.5 (z-mole fraction of the CMC units in the IPCz = [CMC] / [CMC] + [UFR, (PMAG), (PHMG)], and for the CMC- PMAG z = 0.4, CMC-PHMG it is equal to z = 0.6.

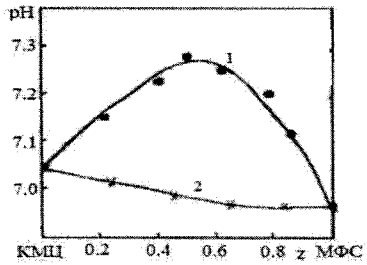



*Fig. 2.4. Changes in the pH of the medium (1) and the hypothetical dependence (2) on the pH of solutions of the mixture of UFR and CMC on the composition in salt-free media. The concentration of the components is 0.01 psi-mole / l. 298 K.*

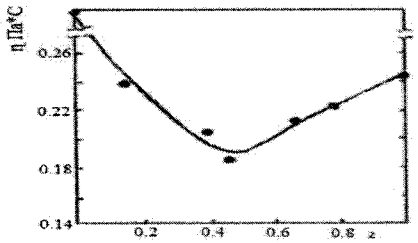
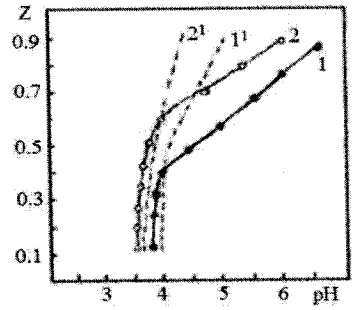



*Fig. 2.5. Dependence of the viscosity change of solutions at 298 K on the ratio of the interacting components z=CMC/CMC+UFR. Concentration C = 0.1 basic mole / l.*






*2.6 Dependence of the composition of mixtures on the pH-medium of CMC with PMAG and PHMG in salt-free media at a temperature of 298 K. 1', 2'- hypothetical dependence, 1,2 - experimental dependence. (1, 1') - CMC-PMAG, (2, 2') - CMC-PHMG*

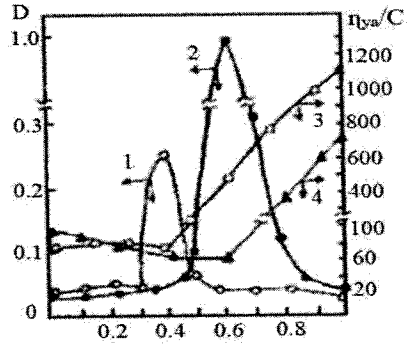



*Fig. 2.7 Dependence of the optical density and reduced viscosity of solutions of polyelectrolyte complexes on the composition in salt-free media. 1,3-CMC-PMAG; 1,4-CMC-PHMG*

Some deviation of the compositions of the IPC CMC-PMAG and CMC-PHMG from equimolar can probably be due to the lack of spatial correspondence of the interacting chemically complementary macromolecules.

The formation of IPC is accompanied by the appearance of compact particles (not only macro, but also possibly nanoparticles), whose appearance is evidenced by the results of measuring the viscosity of CMC-UFR solutions at different ratios (Fig. 2.5). In the formation of IPC, the

fibrillar structure of CMC undergoes changes. This is indicated by the appearance of coil-like structures that arose from the interaction of several dozen molecules [151, 152].

Experiments show that the mixing of aqueous solutions of CMC with PMAG is accompanied by a constant pH to a composition of 0.4 on the curves z = f (pH) (Fig. 2.6, cr.1), then a significant increase is observed. This, in turn, confirms the cooperative nature of the process in the interaction of CMC solutions with PHMG in the composition of mixtures 0.6 (Fig. 2.6, cr.2).

To analyze the experimental data obtained with theoretical calculations, the method proposed in [153] was applied. The composition of the reaction mixture (Z) was calculated by the formula:

$$Z = \frac{(\alpha \cdot S)_{комп}}{(\alpha \cdot S)_{комп} + (\alpha \cdot S)_{полиан.комп}} \qquad (2.1)$$

where α is the degree of ionization of the polyelectrolytes, which was determined as the pH function from the potentiometric titration data. The pKα values for different ionizing groups were obtained from the pH values at the level α = 0.5, the S-degree of substitution of polyelectrolytes. These values are presented in Table 2.1.

Table 2.1.

Characteristics of used polyelectrolytes

| № | Poly-electrolyte | Power of polymerization (PP) | Power of substitution | $RK_\alpha$ |
|---|---|---|---|---|
| 1 | CMC | 650 | 0,8 | 4,3 |
| 2 | PMAG | 20 | 1,0 | 5,9 |
| 3 | PHMG | 400 | 1,0 | 6,4 |

In Fig. 2.6, the theoretical dependences Z = f (pH) (curve 1 for the CMC-PMAG system and curve 2 for the CMC-PHMG system) were also shown. As can be seen from the figure, the theoretical and experimental curves of pH change depending on the composition of mixtures intersect at values of 0.4 and 0.6, respectively CMC-PMAG and CMC-PHMG. This means that the inter-polyelectrolyte complex (PEC) is formed precisely in the indicated component ratios. In other proportions of components a mixture of PEC and one of polyelectrolytes is formed.

Similar results were obtained when studying the reaction of CMC with



PMAG and PHMG. In this case, we successfully applied the method of determining the change in optical density as a function of the component ratio (D = f (Z), Fig. 2.7). Different amounts of polyanion solutions were added to a predetermined amount of polycation and the optical density was measured after complex formation. It was found that the maximum turbidity for PEC CMC-PMAG is observed at Z = 0.4 (Fig. 2.7, cr. 1). In the case of CMC-PHMG, the maximum point corresponds to Z = 0.6 (Fig. 2.7, cr. 2).

We note that the data obtained in the work of potentiometry and spectrophotometry are in good agreement with the results of measuring the viscosity of solutions of mixtures of interacting components (Figure 2.7). The fracture on the curves of the reduced dependence of the viscosity of solutions on the composition is found at a component ratio of 0.4:0.6 for CMC-PMAG and 0.6:0.4 for CMC:PHMG. Adding CMC to a polycation solution having a lower molecular weight, as our studies show, results in a slight decrease in viscosity, which then increases sharply. This is easily explained by the dissociation of the complex, which in turn confirms the possibility of achieving equilibrium in the solution:

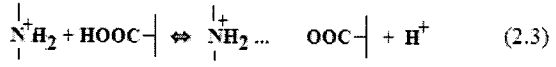
$$CMC + PMAG\ (PHMG) <-> complex \qquad (2.2)$$

It follows from the studies carried out that the composition of the polyelectrolyte complexes CMC-PMAG and CMC-PHMG depends on the nature of the geometric structure and the charge density of the interacting components. We have clearly defined the ratio in which the polymer components react with each other, and the optimum composition of the interpolymer complex was found.

Further, the reactions between weak polyelectrolyte-CMC and PMAG, PHMG, both in acidic media, by charging a polyacid on a positively charged polycation chain, and in alkaline media due to the charging of a polyamine on a negatively charged polyanion chain were thoroughly investigated [154].

Figures 2.8 and 9.9 show curves of potentiometric titration of CMC and mixtures of PMAG, PHMG with CMC (Fig. 2.8), as well as PMAG, PHMG and mixtures of CMC with PMAG, PHMG (Fig. 2-9). The components of CMC with PMAG and PHMG were mixed in acid medium and titrated with alkali. When mixing aqueous solutions of salts of polyamines PMAG HCl and PHMG HCl with CMC, a decrease in the pH of the mixture is observed. Thus, for example, by mixing 0.015 basis mole / liter of CMC solution having pH = 2.8 with equimolar PMAG HCl and PHMG HCl having pH = 3.4, the pH of the mixture becomes 2.55 and 2.4

for CMC- PMAG and CMC-PHMG, respectively (Fig. 2.8). The latter value is set in a relatively short time, i.e. in a few minutes, then saved unchanged. It is in this case that a weak opalescence of solutions is observed. This behavior of a mixture of two polyelectrolytes can be explained by the reaction between polyelectrolytes with the release of protons and the formation of an ionic polyelectrolytic complex according to the scheme [154]:



(2.3)

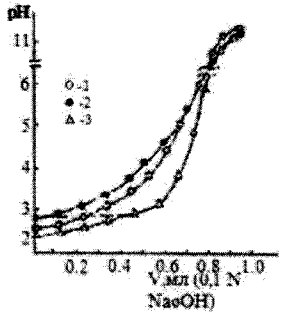



*Fig.2.8. Curves of potentiometric titration of CMC (1) and PEC CMC-PMAG (2), CMC-PHMG(3), concentration 0.01 mole / l (3), concentration 0.01 mole / l.*

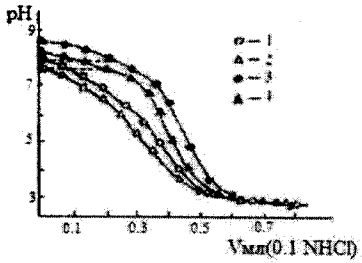



*Fig.2.9. The curves of potentiometric titration of PMAG (1), PHMG (2); PEC CMC-PMAG (3). CMC-PHMG (4).*



We note that the equilibrium of the analogous reaction for low-molecular model compounds is practically shifted to the left.

It is easy to see from Fig. 2.8 that the CMC mixed with the salt of the polymeric base is titrated as a strong acid [155].

In addition to the above-mentioned processes of interaction, unconditional interest is caused by the exchange reactions of the same polyelectrolyte pairs that occur in alkaline media. This reaction can be schematically represented in the following form:

(2.4)

It was observed that similar to the mixing of Na-CMC with PMAG or with PHMG, a decrease in the pH of the solution and the formation of a polyelectrolyte complex were observed.

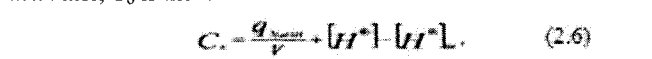
It should be specially noted that an important parameter characterizing the interpolymeric reactions is the degree of conversion in the reaction q, which is the fraction of the intermolecular ion bonds formed from their maximum possible number.

The calculated data in the reactions of these polyelectrolytes are shown in Fig. 2.10. Calculation of 0 was made from potentiometric titration data (from Figure 2.8.2.9) according to the procedure described in [10, 14].

The results of potentiometric titration of mixtures of CMCs with amine-containing polymers, processed as suggested in [10], make it possible to determine the number of ionic bonds between the reacting macromolecules according to the number of protons released in reaction (2.4), depending on the pH of the solution. It is ascertained that to each pH value there corresponds a certain equilibrium value of the degree of transformation θ:

$$\theta = C_к / C_o, \qquad (2.5)$$

where $C_к$ is the concentration of PE links that formed ionic bonds with each other, $C_o$ is the initial concentration of the links of one of the PE:



(2.6)

where $q_{NaOH}$ - amount of added alkali, g-eqv, V-volume of the reaction mixture, l; $[H^+]$- concentration of protons in solution, base-mole / l; $[H^+]_{PC}$ - the concentration of protons in solution created by unreacted polyacid, base-mole / l;

The value of $[H^+]$ was determined by neglecting the polymeric nature of PE and considering the concentration of polyacid or polycations at any

pH equal to the initial value as $\sqrt{K_{ch.pc} C_0}$, where $K_{ch,pc}$ - is the characteristic acid constant dissociation of a polyacid or a poly-base.

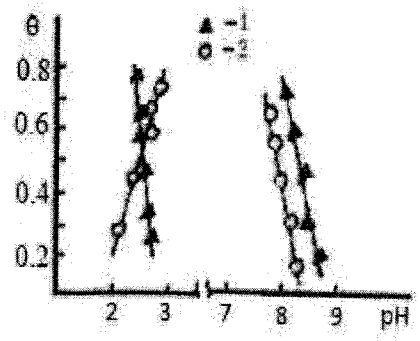



*Fig. 2.10. Dependence of q on pH for the reaction between CMC with PMAG (1), PHMG (2), the concentration of solutions is 0.01 base-mole / l.*

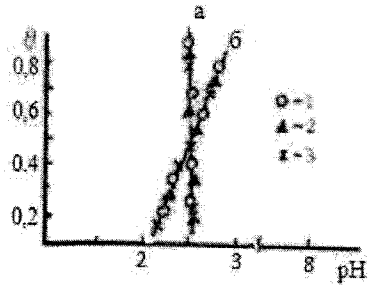



*Fig. 2.11. Dependence of q on pH for the reaction between CMC and PMAG (a), PHMG (b) at different initial concentrations of polyelectrolytes: 1-0.01; 2-0.005; 3-0,002 lb.-mole / l.*

Below we consider in more detail some of the characteristic features of the reduced curves. From Fig. 2.10 that in the acidic region the curves of the dependence of 0 on pH for these PEC pairs cross each other.

The curves corresponding to the same pairs in the alkaline region do not have common touch points. It should also be noted that the slope of the curves 0 = f (pH) in acidic media for complexes is significantly different, which apparently depends on the structure of the reacting macromolecules.



It can also be seen from the curves of the dependence of 0 on pH (Fig. 2.10) that the reactions of formation of polyelectrolyte complexes occur in relatively narrow ranges of pH of solutions, i.e. the reaction between polyelectrolytes is cooperative.

Figure 2.11 shows the dependence of 0 on the pH of the reaction between CMC and PMAG or PHMG at different concentrations of polyelectrolytes ($C_0$-0.01 / 0.001base-mole / l).

These reactions were carried out in aqueous solutions at a temperature of 293 K, while maintaining the equimolar ratio of polyelectrolytes necessarily in acidic media. In this case, the macromolecular chains of practically non-ionized CMC are efficiently charged on polycations of PMAG or PHMG, the process is described by the scheme (2.3). It is seen from Fig. 2.11 that under these conditions, 0 is only a function of the pH of the solution and does not depend on the concentration of macromolecular components. Similar results were obtained in the study of the reactions between CMC and PHMG, also taking place in acidic media. The obtained experimental data are presented in Fig. 2.11.

From the results of calculation of the conversion degree Θ, it was found that the interpolymer reaction between the CMC and the studied amine-containing polymers proceeds within a narrow pH range, i.e. cooperatively PAA.

Now it is known that as a result of processing natural resources, including polymer origin, in industrial conditions, along with the main products, waste is also generated in a rather large amount. So, in the production of phosphorus fertilizers - phosphogypsum, cellulose - lignin, fibers of natural silk - sericin, etc. We note that sometimes these and other industrial wastes are many-tonnage. Ways of their processing with the purpose of obtaining on their basis of new compounds (products, materials, etc.) are found. This is very important from an economic and ecological point of view. We carried out research in this aspect. Below, we will describe the results of using the sericin, the waste of the silk factory of our republic.

The processed technological liquid of the silk-winding production, containing a large amount of valuable sericin protein, is discharged into the sewage system because of the lack of a disposal method.

Sericine of natural silk (SNS) was used as the second component in the complexation of CMCs and the mechanism of intermolecular interactions of SNS and CMC was studied. IPC from SNS and CMC were prepared by a known technique by mixing aqueous solutions of the polymers under study [156].

The presence of carboxyl groups in the molecular chain of CMC and

nitrogen and hydrogen atoms in the SNS polymer facilitated interaction between them and the formation of the corresponding IPC. And the fact that the reaction was actually carried out with the formation of IPC and was confirmed by the potentiometry method. The interaction of polymers in aqueous solutions was accompanied by turbidity, and at high concentrations - even precipitation of IPC.

Figure 2.12 shows the dependence of pH change, reduced viscosity and optical density of IPC solutions based on CMC-SNS on the ratio of components. When the CMC was mixed with a solution of the SNS polycation, a significant increase in the pH of the solution (curve 1) was observed until the ratio of the components of the complex was 1:1 (base-mole /l). The observed kink on the curve indicates the maximum interaction between the components of the IPC [157].

The data obtained by us also agree with the values of the reduced viscosity of aqueous solutions of CMC/CMC + CHN. It is ascertained (cr.2, figure 2.12) that the values of the reduced viscosity decrease to a composition of 1:1 and remain unchanged. The inflection points on the viscosity curves correspond to the composition of the maximum yield of the interpolymer complex Z, which can be explained by possible conformational transformations in the formation of a complex compound of the sericin protein with CMC. And further preservation of the viscosity value of solutions of mixtures at Z1 ratios is obviously connected with the presence in the system of excess SNS, which is not bound in the complex.

Very similar results were observed in the study of the reaction of CMC with SNS by the method of changing the optical density from the component ratio (D = f (Z)) (cr.3, Fig. 2.12). During the experiments, different amounts of polyanion solutions were added to a certain amount of polycation, then, after complex formation, their optical density was measured. It is easy to see from Fig. 2.12, cr.Z, that the maximum turbidity for the IPC CMC-SNS corresponds to the value Z = 1.

The IR spectra of the products obtained by us also confirm the chemical interactions of CMC with SNS. Thus, in the IR spectrum, the bands in the region of 1740 $cm^{-1}$, characteristic of the H bond of the IPC, are clearly exposed. The IR spectra of the CMC (curve 1) obtained at pH = 2.5 are given in Fig. 13.13. The presence of a band in the initial CMC at 1710 $cm^{-1}$ is characteristic of the COOH group. The shift of the absorption band of νCO observed in the figure to the high-frequency region by 30-40 $cm^{-1}$ is due to the presence of H bonds between the carboxyl groups of H-CMC (COOH), $NH_2$-groups of SNS (curve 2).

From the above-mentioned results of the research it follows that complex studies confirmed the formation of polymer-polymer complexes in



[redacted] following systems: CMC:UFR = 1:1, CMC:PMAG = 0.4: 0.6, CMC: [redacted] 0.6: 0.4 and CMC:SNS = 1:1. So, we can conclude that the [redacted] interactions of CMCs with different polycations can be either IPC, [redacted] of IPC and one of the polymers - CMCs and molyations.

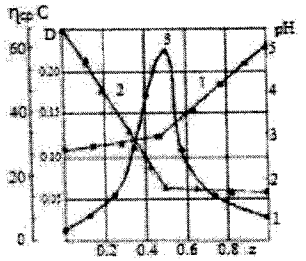



*Fig. 2.12. Dependence of the change in pH (1) of the reduced viscosity (2) and the optical density (3) of IPC solutions on the basis of CMC-SNS on the ratio of components at 298 K.*

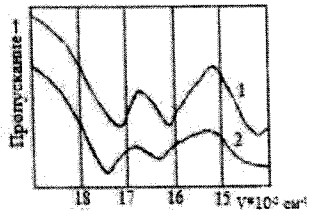



*Fig. 2.13. IR spectra of CMC (1) obtained at pH = 2.5, and the IPC of CMC-SNS (2).*

### 2.3. Water-soluble complexes based on carboxymethylcellulose

The study of water-soluble IPCs from a scientific point of view is of interest for creating a unified approach to describing the equilibrium, kinetics and mechanism of reactions between heterogeneously charged polyelectrolytes, accompanied by the transfer of polyions, as well as a complex evaluation of the structure and properties of the IPCs formed. At the same time, it should be pointed out that the preparation of water-soluble IPC requires compliance with certain conditions, the ratio of the initial components, the pH of the medium. Otherwise, products of the

stoichiometric complex in the form of a precipitate and a supernatant solution consisting of IPC or one of the components will inevitably arise.

Hydration of IPC is limited not by the elasticity of the grid and is determined not by entropic factors, as for ordinary high-molecular compounds, but depends on such characteristics of polycomplexes as the degree of conversion in the interpolymer reaction and the composition of IPC [76, 77, 158]. These same parameters to a large extent determine the properties and structure of materials from the IPC. In hydrogels formed by a pair of strong polyelectrolytes (PE), a correlation is observed between the composition of the IPC and its swelling in water.

The authors of this monograph carefully studied the dependence of the equilibrium water content in the IPC of CMC-UFR, CMC-PMAG, CMC-PHMG and CMC-SNS on the ratio of interacting components (Fig. 2.14). In the figure, for comparison, similar literature data are given [77]. The minimum amount of water is contained in stoichiometric IPC gels. In IPC, formed by weak PE, there is a different picture. For example, the enrichment of PAA-PEI with a poly base is accompanied by an increase in the hydration of the gel, and with polyacid - a decrease in the moisture content [158,159]. Low swelling in water is due to the formation of hydrogen bonds, which lead to an additional structuring of IPC gels [158].

In IPC, enriched with CMC and polycation, as shown in Fig. 2.14, water is mainly in a bound state. In the stoichiometric IPC, the total water content and the proportion of free water are low. We point out that, since the water-swelling properties of IPC depend on the nature, the type of bonds and the geometric structure of the interacting components, and also the ability to swell in aqueous media [158], we also studied the dependence of the degree of IPC swelling in aqueous media on the ratio of interacting components. The data obtained are shown in Fig. 2.15.

These data suggest that the inclusion of an excess amount of CMC in the IPC (Z> 0.5) leads to an increase in the degree of swelling of the IPC of CMC-UFR (curve 1), while the introduction of an excess of UFR (Z <0.5) is accompanied by a decrease in their swelling .

The picture described above is also observed in the IPC CMC-SNS (curve 4). In the complexes CMC + PMAG and CMC-PHMG at an equimolar ratio of the interacting components, the swelling is the smallest. With an excessive amount of one of the components (CMC or PMAG, PHMG), the swelling is increased to a certain limit (see 2, 3). The change in the degree of swelling of these IPCs can be explained by the fact that in the IPC at an equimolar ratio of components the interaction between their macromolecules is greatest. In other words, ionic bonds are observed between CMC and PMAG, PHMG. Under these conditions, the presence of



free polar and ionic functional groups of one or another component included in the polycomplex in excess will certainly increase the swelling of the films. The increase in swelling is naturally associated with the presence of free carboxyl groups [73].

The experiments also confirmed that when the concentration of PMAG and PHMG increases in CMC up to their equimolar ratio, interchain ion bonds are formed. In this case, there is a decrease in the number of unbound functional groups in the CMC, which largely prevents the swelling of the systems (Fig. 2.15).

An interesting fact was revealed: polycations of PMAG and PHMG do not themselves swell in water. However, their presence in the IPC in excess, relative to the equimolar, will contribute to an increase in the swelling of the system. Obviously, this is due to the content of protonated amino groups of PMAG and PHMG in the system. These results are in good agreement with the data of the equilibrium water content in the IPC (Fig. 2.14).

It is important to note that in the equilibrium-swollen state, depending on the ratio of the interacting components, the general regularity of the modulus of elasticity is observed, however, the numerical values of this characteristic are different. These data are shown in Fig. 2.16. Comparing the curves 1-4 in Fig. 2.16, one can judge the dependence of the initial modulus of elasticity E of the IPC on composition, which is the opposite of the equilibrium water content (Figure 2.14).

In the case of an equilibrium-swollen state of the film of the interpolymer complex, water molecules easily break weak (van der Waals) and easily accessible hydrogen bonds [160]. At the same time, the energy of the interchain ion bonds decreases [14, 73], which ultimately leads to a general decrease in the modulus of elasticity of the obtained IPCs and their composites in the swollen state in comparison with air-dry [122].

It can be concluded that with a change in the content of the polyanion and polycation in the IPC, a drop in the E values is observed (Fig. 2.16), which indicates the identity of the IPC with the IPC samples based on PAA and flexible-chain polyamines [161, 162]. For the latter, the dependence of E on the composition passes through a maximum in the region Z ~ 0.3 3 [158].

In the case of pure CMC, the main links between the macromolecules are hydrogen ones, in the IPC CMC-UFR various: hydrogen and interchain ionic bonds, and in the case of IPC CMC-PMAG and CMC-PHMG - only ionic bonds. Under the action of water molecules, hydrogen bonds break in both the CMC and the IPC, however, in the IPC, the ionic bonds remain unbroken.

A slight decrease in the modulus of elasticity of the CMC-UFR system and CMC-SNS (cr. 1 and 4), based on the above research results, can be explained by some plasticizing action of water molecules. About this and in the literature there are certain statements [14].

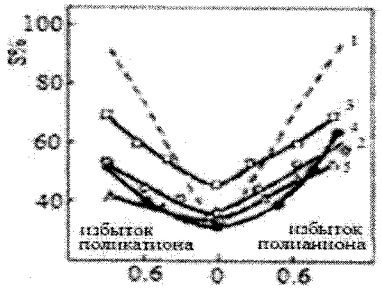



*Fig.2.14. The equilibrium water content of the IPC: 1-polystyrene sulfonate sodium (PSSNa) -polydimethylammonium chloride (PDMACl) [77]; 2-CMC-UFR; 3-CMC-PMAG; 4-CMC-PHMG; 5-CMC-SNS. At 298 K.*

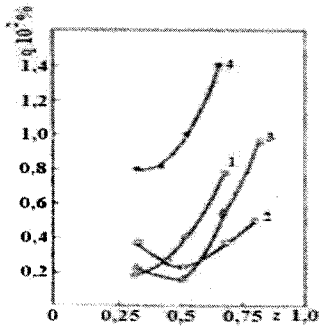
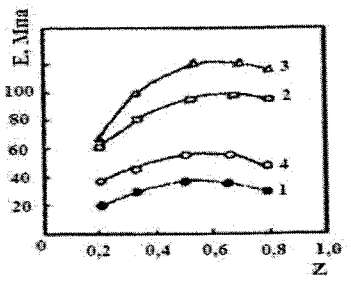



*Fig.2.15. Dependence of the degree of swelling of IPC on the composition in water at pH = 6. 1-IPC CMC-UFR; 2-CMC-PMAG; 3-CMC-PHMG; 4-CMC-SNS.*






*2.16. Dependence of the elastic modulus E of IPC films in the equilibrium-swollen state in aqueous media (pH = 6) at 298 K from the ratio of the initial components: 1-CMC-UFR; 2-CMC-PMAG; 3-CMC-PHMG; 4-CMC-SNS.*

Thus, it can be concluded that the formation of heterogeneous structures in the IPC-CMC or IPC-UFR, PMAG, PHMG and SNS systems results in an uneven load distribution. This is clearly indicated by a decrease in the modulus of elasticity of the samples studied.

On the basis of the data obtained, it can also be concluded that the structure of the CMC-UFR, CMC-PMAG, CMC-PHMG, and CMC-SNS systems studied by us seems to be intermediate (at the junction) between the structure of composite materials, where the components are not linked by chemical bonds and the structure of interpolymer complexes in which the bond between polymer chains is provided by cooperative interchain ion or hydrogen interaction.

## 2.4. Physical properties of interpolymer complexes based on carboxymethyl cellulose and amine-containing polymers

A number of physical characteristics of polyelectrolytes from mixtures of acidic and basic polymers deviate from additivity, which confirms the interaction between the polymers (Fig. 2.4). Formed IPC in its physical properties, is very close to amorphous compounds. This is indicated by the nature of the change in the thermal conductivity ($\chi$) of the IPC as a function of temperature in the range 300-500 K. In our experiments it was found that traditional methods for studying thermophysical properties are not suitable for studying the thermal conductivity of thin films because of the relaxation nature of any processes occurring in polymers, i.e. thermophysical changes.

In connection with the above-mentioned, in our opinion, the study of such phenomena as the propagation and absorption of heat associated with

the dynamics of macromolecules must be carried out by the method of short-period periodic heating using a low-inertia probe [163]. The resulting thermal conductivities will certainly be free of the relaxation contribution and will mean purely molecular thermal conductivity.

Figure 2.17 shows the temperature dependence of the thermal conductivity of four samples: 1-source CMC; 2-IPC CMC-UFR; 3-CMC-PMAG; 4-CMC-PHMG.

We can note the following features of the behavior of the thermal conductivity $\chi$ as a function of temperature: in the 300-500 K range, with an increase in temperature, $\chi$ (T) has a gentle rise. This can be explained by the predominant contribution to the heat capacity of the longitudinal acoustic branch of the oscillations. In the 350-400 K region, $\lambda$-shaped peaks are observed, and with further increase in temperature the thermal conductivity increases linearly. Here it should be noted that the thermal conductivity for the CMC-UFR complex (Fig. 2.17, cr. 2) varies smoothly and there is no peak. This indicates that the influence of ionic and hydrogen bonds on the thermal conductivity is of great importance in the complex of CMC-UFR. It should be noted that the curves are well reproduced with both temperature increase and reverse scanning.

The region of $\lambda$-shaped behavior of $\chi$ can apparently be related to the change in the conformation of glucopyronous rings contained in various cellulose derivatives at 330-340 K [164, 165]. In the formation of IPC CMC-PMAG, CMC-PHMG, the carboxylate anionic group of CMC and the amino group of PMAG and PHMG are reacted, which results in interpolyelectrolyte ionic bonds [166]. It should be noted that the magnitude of the jump (indicated in Fig. 2.17 by a stroke) in the complexes characterizes the growth of the energy of interpolymer bonds. There is no jump in the original CMC. The width of the anomalous peak determines the spectrum of oscillations of macromolecules, which depends on the complexity of its structure. The displacement of anomalies in the low temperature region may be due to a lower degree of polymerization of the polycation of PMAG.

We point out that with an increase in the degree of polymerization of the polycation represented by the above IPC, an increase in c is observed (see the range 400-500 K), which agrees well with the semi-empirical Ayerman model [164], according to which:

$$\frac{1}{\chi} = \frac{1}{\chi_\infty} + \frac{A}{M}, \qquad (2.7)$$

where, $\chi$ is the thermal conductivity of a polymer of an infinitely large molecular mass M, and $\Lambda$ is a constant.



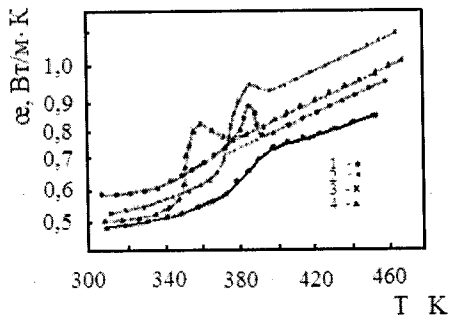



*Fig. 2.17. Temperature dependence of thermal conductivity from thin films: 1-initial CMC; 2-CMC-UFR; 3-CMC-PMAG; 4-CMC-PHMG.*

On the basis of these experiments it can be concluded that the presence of interpolymer bonds contributes to an increase in resistance along the chain. Therefore, the spread of c for the presented complexes was found not to exceed 15%. Further, we note that the increase in thermal conductivity in the 300-500 K range is characteristic for most amorphous polymers and reduces mainly to the temperature dependence of $C_V$ (T). Since in polymers the mean free path of phonons 1 is comparable with the length of macromolecules and does not change with temperature, the average propagation velocity of phonons $\theta$ depends weakly on temperature [167]. Hence, proceeding from the basic kinetic formula:

$$\chi = 1/3\rho C_v \vartheta l, \qquad (2.8)$$

The latter changes according to the linear law [167]:

$$C_v = 1{,}5R\pi^2(T/\theta_1) \qquad (2.9)$$

in a wide temperature range, $\theta_3$ "T" $\theta_1$, where $\theta_1\theta_3$- mean the corresponding characteristic temperatures of the skeleton oscillations of the macromolecule (one-dimensional continuum) and the three-dimensional continuum.

It is known [168, 169] that on the current-voltage characteristic (CVC), the analysis of which is the most accessible method for studying various structures, the specific current-carrying regime manifests itself in the form of a section with a definite dependence. Therefore, the detection of current transmission at sufficiently large currents of the regime, greatly

facilitates their evaluation. For our structures based on interpolyelectrolyte complexes (IPEC), this identification was carried out using the existing analogy between the phenomenological description of the electronic and ionic conductivity and the quasi-chemical description of the interaction of crystal lattice defects with each other with imperfection and the surface of the resulting material.

The known theoretical results [170-172] were used for the analysis of the current-voltage characteristics of the sandwich metal-IPEC metal structures made on the basis of CMC and amine-containing polymers (UFR, PMAG and PHMG). Under the conditions of our experiment, contact material was nickel (Ni), deposited by thermal evaporation in a vacuum of 5-10-5 Torr. In the voltage range V = 10 -1 -102 V, in the experimental CVC were described by dependences close to the Ohmic J ~ Vn, n = 1 (Fig. 2.18).

The absence of superlinear sections indicates an insignificant effect of the injection of current carriers from the contact, the absence of sublinear ones has a negligible effect on the contact regions of the space charge (003), including those associated with the metal-IPEC transition layer. The times of current relaxation to a stationary value are less than expected for ionic conductivity, i.e. at the indicated stresses, the structures studied exhibit the properties of an ionic high-resistance semiconductor with ohmic contacts to it.

It can be concluded that the extended Low diagram represents the basis of the phenomenological picture of the contact phenomena for both the ionic conductivity type and the quasichemical interaction of the defects. In particular, this fully applies to structures based on polyelectrolyte complexes.

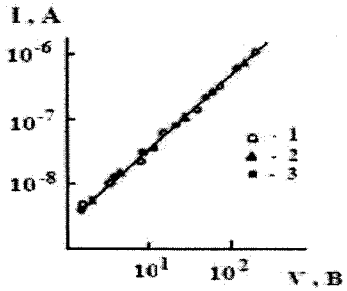



*Fig. 2.18. A typical experimental CVC of metal-IPC-metal structures based on the interpolymer complex CMC-UFR (1), CMC-PMAG (2) and CMC-PHMG (3), at a temperature of 298 K.*



To determine the conductivity mechanism, DC conductivity measurements and the response of the C-IPC-C electrochemical cell with ideally polarized blocked (for ions) electrodes (C-graphite) to the pulsed signal were made. Based on the results of the studies, it was concluded that the ionic conductivity occurs in polymer films of the IPC CMC-UFR, CMC-PMAG, and CMC-PHMG. The polarization of the cell with the application of a constant electric field E = 0.3 V / m (T = 300 K) occurred for 1000 s, while the external field (partially, by 90%) is blocked by a double electric layer formed on the electrode surface of the sample mobile ions ($Na^+$, $OH^-$, $H^+$).

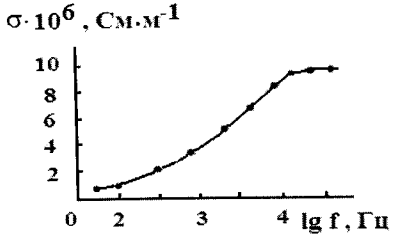



*Fig. 2.19. Frequency dependence of electrical conductivity CMC film obtained at pH 2.5, T-300 K.*

Figure 2.19 shows the frequency dependence of the electrical conductivity s of the CMC film. At low frequencies (<10 kHz), mobile ions reach the surface of the sample and create a double electric layer that prevents further transfer to the surface of ions from the interior regions of the sample, as a result of which the total conductivity decreases. Therefore, to measure the electrical conductivity, a frequency of 10 kHz was chosen, above which the electrical conductivity changes insignificantly. In the case of complexes CMC-PMAG, CMC-PHMG and CMC-UFR, a similar pattern is observed.

It is known that the effect of temperature on electrical conductivity is clearly reflected in the physical state of CMC and IPC on its basis. The experimental data shown in Fig. 2.20 show that the temperature dependence of lgσ over a wide range of variation of T is nonlinear. Only in a relatively narrow temperature range are the Arrhenius character [168]. In this case, the activation energies E of the electrical conductivity of the CMC-PMAG and CMC-UFR complexes coincide and amount to 53.5 kJ/mole, and for the CMC-PHMG complexes E = 71.3 kJ/mole.

We found that the activation energy of the electrical conductivity for

the initial CMC is 20 kJ / mole. Such a small value for CMC, apparently, is due to a relatively high local molecular mobility. The presence of breaks σ = f (T) at ~ 300 K indicates the ionic character of the conductivity of the samples [173]. The kinks in the 500 K region are associated with the thermal destruction of CMC and IPC. In a detailed analysis of the results obtained, in addition to ionic conductivity, it is also necessary to take into account the contribution of the through-current and electronic conductivity [168].

To investigate the relaxation processes in CMC and IPC samples, dielectric properties using field electrodes (molybdenum electrodes insulated with mica plates 0.01 mm thick) were further studied [174]. The results of measuring the temperature dependences of the permittivity ε' and the dielectric loss tangent tgδ for the samples of the initial CMC are presented in Fig. 2.21.

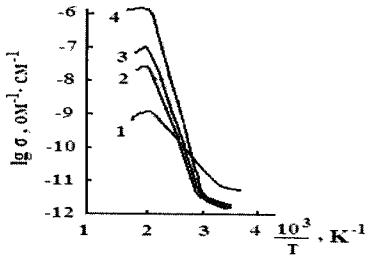



*Fig. 2.20. Dependence of electrical conductivity on temperature for samples obtained at pH 2.5: 1-CMC; 2-CMC-UFR;3-CMC-PMAG; 4-CMC-PHMG. f = 10 kHz.*

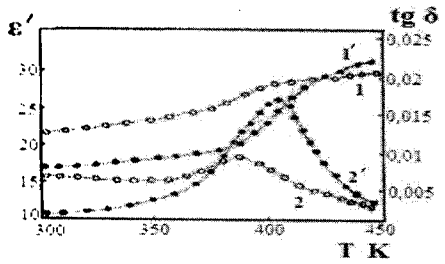



*Fig.2.21. The temperature dependences of the dielectric loss tangent tgδ (1, 2) and the permittivity ε '(1', 2 ') in the initial CMC, 1, 1' for the second scan, 2, 2 'for the first. pH 2.5, f - 10 kHz.*



These data indicate the influence of moisture sorbed by the sample on the dielectric properties. Thus, for air dried at 388 K CMC film, which contains sorbed moisture, a peak tg8 is observed (Fig. 2.21, curve 2). In such samples, the water molecules form hydrogen bonds with the primary hydroxyl groups of CMC macromolecules [175]. When the samples are repeatedly scanned, heated to 450 K, the peak tg8 shifts to a higher temperature region and an intense peak tgδ is observed at 405 K.

Studies of the temperature dependence of ε' in the subsequent heating cycles indicate that the region of abrupt change in ε' also shifts toward higher temperatures when the samples are heated. The observed results are shown in Fig.2.21, cr. 1 'and 2'.

The observed effects are explained by the partial evaporation of sorbed water upon heating the samples to 450 K in the first thermal cycle. As it is known, water molecules in the case of CMC act as a plasticizer. It can be assumed that this is quite feasible for IPC based on the CMC [14]. Therefore, with a partial evaporation of the water, the relaxation transitions in these polymers shift to higher temperatures.

Further, we also note that all the described processes are completely reversible. Consequently, the dielectric characteristics of warmed CMC and IPC samples are restored after sorption of water and when the samples are held in air at room temperature. Along with this, it can be pointed out that subsequent displacements of the maxima of tgδ will occur in the region of higher temperatures.

Figure 2.22 shows the temperature dependences of ε 'and tgδ of CMC-PMAG complexes (curves 1 and 1'), CMC-PHMG (curves 2 and 2 ') and CMC-UFR (curves 3 and 3') heated at 423 K in for 1 hour in the air. The shape of the curves shown in Fig. 2.22 is characteristic of the Debye mechanism of relaxation of freely charged carriers. The observed dispersion of the dielectric constant can be explained in terms of the model of thermal ion polarization [176].

It was noted above that the IPCs formed as a result of the interaction of CMC's with PHMG, PMAG and UFR are new interpolymer compounds whose properties, as a rule, differ greatly from those of their constituent polymers. This can be seen, including when studying the dielectric characteristics of IPC.

It is seen from Fig. 2.22 that the position of the maxima of tgδ for the IPC is shifted to low temperatures relative to CMC, for which the maximum is observed at 405 K. For the CMC-PMAG complex, the maximum of tgδ corresponds to a temperature of 348 K, for the CMC-UFR complex - 375 K. At the same time, the values of ε 'and tgδ themselves increase by a factor of ~ 10. We also note that the presence of hydrogen

bonds in the complex CMC-UFR between COOH groups CMC and> C = 0 by UFR groups [133], in addition to inter-polymer ionic bonds, significantly limits the segmental mobility of macromolecules included in the IPC. This is reflected in the fact that the values of ε 'and tgδ for the CMC-UFR complex turn out to be the smallest in comparison with other IPCs, in which the hydrogen bonds are absent.

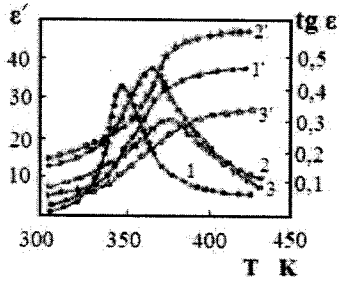



*Fig. 2.22. The temperature dependences of the dielectric loss tangent* tgδ *(1-3) and the permittivity ε '(1'-3') of CMC-PMAG samples (1,1 '), CMC-PHMG (2, 2') and CMC-UFR (3 , 3 ') obtained at pH2.5, heated at 423 K for 1 hour in air. F = 10 kHz.*

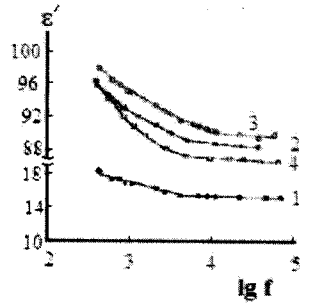



*Fig.2.23. The frequency dependences of the permittivity ε 'in the initial CMC (1) and the complexes CMC-PMAG (2), CMC-PHMG (3). CMC-UFR (4), obtained at pH 2.5, T = 300 K.*



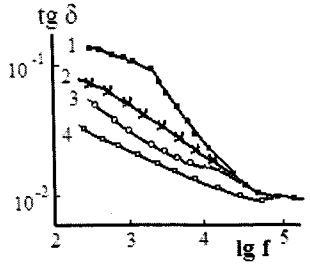



*Fig. 2.24. The frequency dependences of the dielectric loss tangent tgδ in the initial CMC (1) and the CMC-PMAG complexes (2), CMC-PHMG (3), CMC-UFR (4) obtained at pH 2.5, T = 300 K.*

Further, the frequency dependences of the permittivity of the CMC-PMAG complexes, CMC-PHMG, CMC-UFR (curves 2-4) and CMC (curve 1), shown in Fig. 2.23 were studied. It is seen that as the frequency of the electric field is lowered, the dielectric constant of the IPC samples appreciably increases, which is apparently due to the Maxwell-Wagner polarization [177].

Studies of the frequency dependence of the tgδ complexes of CMC-PMAG, CMC-PHMG, CMC-UFR and the original CMC showed that the tgδ values of the IPC are noticeably lower than the CMC in the frequency range ~ 104 Hz (Fig.2.24). This reflects the change in the nature of molecular mobility as a result of the formation of IPC. At the same time, curve 4 for the CMC-UFR complex lies below curves 2 and 3 corresponding to the complexes CMC-PMAG and CMC-PHMG. This, as in the discussion of the temperature dependences of ε 'and tgδ, can be explained by the presence of interpolymer hydrogen bonds in the complex CMC-UFR in addition to the ionic ones.

Thus, the presence of ionic conductivity and a significant difference in the electrophysical properties of the CMC and the corresponding IPC significantly expands the areas of their application, for example, the possibility of creating sensitive moisture sensors based on the IPC studied.

## 2.5. Thermodynamics of carboxymethyl esters of cellulose polycomplexes formation with various polycations

Let us recall once again that the objects of research are interpolymer complexes and composites based on carboxymethylcellulose with different polycations and their compatibility. It is pertinent to indicate that these polymers are interesting by the complex structure caused by the presence of

- COONa, -COOH, -OH, -CO, -NH and -$NH_2$ - groups in the chain. Thanks to these and other characteristics, interesting results were obtained in thermodynamic studies.

Sorption ability of IPC and composites based on CMC, it can be noted, is related to their structural features. Compatibility of polymers in this system is determined, mainly, by their average free energy of mixing.

In Fig. 2.25 water sorption isotherms of interpolymer complexes of CMC-UFR, CMC-PMAG and CMC-PHMG, as well as CMC isotherms are presented. The greatest sorption ability is possessed by composites, the least-interpolymer complexes of stoichiometric composition, obtained with the volume ratio of CMC:UFR = 0.6:0.4, CMC:PMAG = 0.4:0.6 and CMC:PMGH = 0.6:0,4. With the increase in the content in the polycomplex of UFR, its sorption caPAAity is markedly increased. Very interesting isotherms, corresponding to complexes CMC:UFR = 0.6:0.4, CMC:PMAG = 0.4: 0.6 and CMC:PHMG = 0.6:0.4. The decrease in sorption capacity is due, apparently, to the condensation of the structure of the polycomplexes and to the growth of the packing density of macromolecules consisting of chains of various polymer components of different chemical nature and their affinity for each other. It is this position and the corresponding isotherm that will accurately reflect the complex sorption mechanism, namely, the sorbate and sorbent molecules associated with the chemical structure, as well as the flexibility of the chains and the sorbent structure. These statements are confirmed by data on the change in the structure of the products of the polycomplex and composite, obtained by electron microscopy [122] and swelling (Fig. 2.15).

It is known [178] that the adsorption process on microporous systems proceeds according to the mechanism of volume filling. Therefore, adsorption isotherms are described by the equations of the **theory of volume filling of micropores** (TVFM). Using the positions of the TVFM and generalizing a large experimental material, we came to the conclusion that it is possible to apply the Weibull distribution function as a distribution function of the adsorption volume from the potential value for describing adsorption on polycomplexes. With respect to the distribution of the degree of filling by the adsorption potential, the Weibull distribution function is represented by the correlation:

$$\theta = \exp\left[-(A/E)^n\right], \qquad (2.10)$$

where E and n are parameters independent of temperature. The value E is called the characteristic energy of adsorption. The exponent n is expressed by



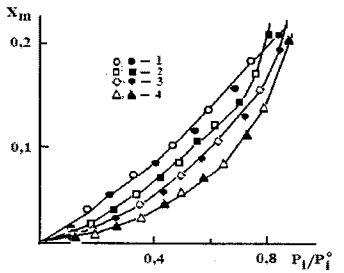



*Fig.2.25. Isotherms of water vapor sorption by polymers CMC (1) complexes CMC-UFR (2), CMC-PMAG (3) and CMC-PHMG (4).*

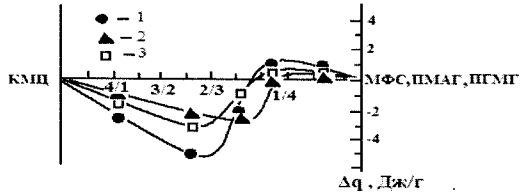



*Fig. 2.26. Dependence of the average free mixing energy (Dgx) on the composition of CMC-UFR complexes (1), CMC-PMAG (2) and CMC-PHMG (3).*

Integers depending on the structure of the adsorbent. A is the work of adsorption, i.e. the work of transferring 1 mole of gas from the surface of a liquid adsorbate

$$A=RT\ln(P_i/P_i^\circ). \qquad (2.11)$$

The degree of filling of the adsorbent can be represented as the ratio of the adsorption amount x/m to the maximum adsorption (x/m) o. Then from equation (2.10) we obtain:

$$\frac{x}{m}=\left(\frac{x}{m}\right)_o \exp\left[-(A/E)^n\right] \qquad (2.12)$$

Equation (2.12) is a general equation of the TVFM. In the logarithmic form, it has a linear form:

$$\ln\frac{x}{m}=\ln\left(\frac{x}{m}\right)_o-\frac{A^n}{E^n}. \qquad (2.13)$$

In a number of papers, M.M. Dubinin and other authors [179,180], cases of distribution of micropores depending on various factors were considered. At the same time, it was suggested that it is advisable to use both the two-term and three-term TVFM equations.

Adsorption isotherms for the samples we study can be described by the single-term TVFM equation:

$$\frac{x}{m} = \left(\frac{x}{m}\right)_{01} \exp\left[-(A/E_{01})^{n_1}\right] \qquad (2.14)$$

where x/m is the adsorption values in mmole /g, $A=RT\ln P_i/P_i^\circ$ - the adsorption work in kJ / mole.

The isotherms of water adsorption on CMC and complexes, calculated by TVFM, are shown in Fig.2.25. For the water-CMC system, the parameters of equation (2.14) are: $(x/m)_{01}$=0,186 mmole / g,$E_{01}$=1,787 kJ / mole, $n_1$=1 and the TVFM equation becomes:

$$\frac{x}{m} = 0{,}186\exp\left[-(A/1{,}787)^1\right] \qquad (2.15)$$

for the complex CMC-UFR: $(x/m)_{01}$=0,603 mmole /g, $E_{01}$=0,25 kJ /mole, n =1/2 and the TVFM equation:

$$\frac{x}{m} = 0{,}603\exp\left[-(A/0{,}25)^{\frac{1}{2}}\right] \qquad (2.16)$$

for complex CMC-PMAG: $(x/m)_{01}$=0,24 mmole/g, $E_{01}$=0,92 kJ/mole, $n_1$=1 and the TVFM equation:

$$\frac{x}{m} = 0{,}24\exp\left[-(A/0{,}92)^1\right] \qquad (2.17)$$

for complex CMC-PHMG: $(x/m)_{01}$=1,86 mmole/g, $E_{01}$ =0,0224 kJ/mole, $n_1$ 1/3 and the TVFM equation:

$$\frac{x}{m} = 1{,}86\exp\left[-(A/0{,}0224)^{\frac{1}{3}}\right] \qquad (2.18)$$

On the basis of the obtained data (Fig. 2.25), it can be concluded that the calculated data are in good agreement with experimental data (where o,,◊,Δ· experimental points, a•,■,♦,▲ -calculated on the basis of equation TVFM). In addition, it should be noted that the water in the systems under investigation is distributed uniformly on the surface and shows the composition of the structure of the polycomplex, and in the case of CMC,



[illegible] densified due to hydrogen bonds.

According to the data of water sorption by homopolymers and [illegible] by the equation proposed by A.A. Tager [3], we calculated the [illegible] mixing energy (Δgx), the minimum value of which corresponds [illegible] polycomplex (Figure 2.26).

Based on the measurement of the heat of swelling, the average [illegible] of mixing Δhx was calculated using the following equation:

$$\Delta g_x = \Delta h_x - T\Delta S_x, \qquad (2.19)$$

The entropy of mixing homopolymers and polycomplexes is [illegible], the data obtained are given in Table. 2.2.

Table. 2.2.

**Thermodynamic parameters of complexes**

| Complexes and their correlations | $-\Delta h_x$, kJ/mole | $-T\Delta S_x$, kJ/mole |
|---|---|---|
| CMC:UFR = 0.6:0.4 | 24 | 18,7 |
| CMC:PMAG = 0.4:0.6 | 16 | 13,4 |
| CMC:PHMG = 0.6:0.4 | 19 | 16,0 |

The results of studies of thermodynamic properties indicate that the complexation of CMC-UFR, CMC-PMAG and CMC-PHMG is accompanied by negative changes in Δhx and TΔSx mixing. This is a very important condition for the thermodynamic compatibility of polymers, indicating the formation of hydrogen or electrostatic bonds between the functional groups of the interacting components.

Thus, it can be concluded that polycomplexes of stoichiometric composition based on CMC-UFR, CMC-PMAG and CMC-PHMG are a particular case of polymer mixing, when interpolymer bonds arise between heterogeneous macromolecules. All the results of thermodynamic studies obtained by the authors of this monograph, IPC and composite samples indicate the validity of these conclusions.

## 2.6. Mechanical properties and the effect of conditions for the preparation of films of an interpolymer complex on their performance characteristics

As was noted, a new class of polymeric materials - interpolymer complexes - reveal a number of valuable properties and are already applied

in some branches of technology, in medicine and agriculture. However, the rich opportunities presented by interpolymer complexes are currently being realized only to an insignificant degree, which is due to the lack of large-capacity polyelectrolytes and systematic data on their properties, since most of the studies were aimed at establishing the kinetic regularities of the complexation reaction [12,14,15, 32, 57,137].

In connection with this, the study of the properties of interpolymer complexes and the identification of the relationship between the properties of products and the properties of interacting components has acquired a particularly great practical and scientific value at the present time. The solution of a number of scientific issues specific to interpolymer complexes makes it possible to obtain new polymer products with specified properties. Meanwhile, studies in this direction are few and performed for a small number of systems, such as polyelectrolyte complexes (PEC) [7,56,73] and polycomplexes (PC) [16,23]. Interest in the study of the mechanical properties of IPC films is due to the urgency of the problem of their application in medicine, agriculture and water management, and in soil melioration.

Typical curves of uniaxial stretching of IPC films with different structures are shown in Fig. 2.27. It can be seen that CMC and IPC films have elastic deformation in a small interval - up to 15%. From the literature data it is known [181] that cellulose ethers, including CMCs, are in the air-dry state at room temperature in a vitreous state, therefore, in the uniaxial tension diagram (Fig.2.27, cr.5), there is a small area of high-elastic deformation. A comparison of the deformation-strength curves of CMC and IPC shows (compare to 1-4 and 5) that they are of the same type in their deformation-strength properties and, obviously, are in the same physical state, i.e. in the glassy. This is not surprising, because IPC, essentially represent microheterophase systems in which the role of the continuous phase is played by the CMC. This agrees with the data of the paper [48].

Dynamometric curves (Fig.2.27), because of small values of deformation, do not give a complete picture of the structure of the objects under study. Therefore, in order to evaluate the structure of IPC films with different ratios of the original components, it was necessary to determine the modulus of elasticity, the value of which depends on the structure of the interacting components and the frequency of interchain macromolecular interactions. For polymers in the vitreous state, the elastic modulus (E) is determined mainly by the intermolecular interaction energy [181], so its value should depend on the nature and intensity of interpolymer interactions.

With an increase in the number of polycations in the IPC system to an



equimolar composition, the intermolecular interaction of CMCs and polycations increases and the kinetic flexibility of the CMC macromolecules decreases. This is expressed in the strengthening of the elastic properties of the polymer material, which is confirmed by the growth of the elastic modulus (Fig. 2.28). The maximum modulus of elasticity, and hence of mechanical properties, is accounted for by the equimolar composition of the components. With a further increase in the number of polycations in the system and the volume fraction of the dispersed phase, the modulus of elasticity again decreases.

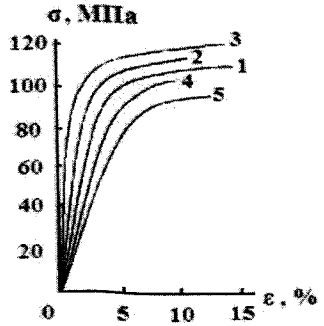



*Fig.2.27. Deformation-strength curves of IPC films in air-dry state at 298 K: 1-CMC-UFR; 2-CMC-PMAG;3-CMC-PHMG; 4-CMC-SNS; 5-CMC.*

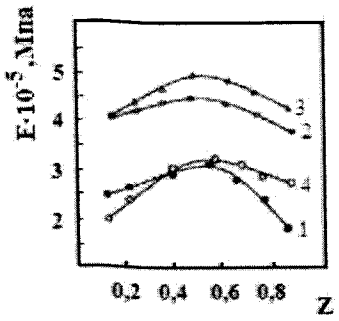



*Fig. 2.28. Dependence of the elasticity modulus E of IPC films in the air-dry state at 298 K on the ratio of the interacting components: 1-CMC-UFR; 2-CMC-PMAG; 3-CMC-PHMG; 4-CMC-SNS.*

When the IPC is formed, a conformational change occurs in the macromolecules of the constituent components of the polymer-polymer complexes and the compacting of the interacting macromolecules is combined with the formation of double-stranded coil-like structures and particles of the polycomplex. If there is an excessive amount of CMC or polycations in the IPC film, the films have a heterogeneous structure.

In practice, IPC films as anti-filtration screens, etc. will be used in the water-swollen state. Therefore, the most important was to study the physico-mechanical properties of materials from the IPC in an equilibrium-swollen state. These properties are shown in Section 2.3 in Fig. 2.16.

Interpolymer complexes of CMC-UFR are stabilized by interchain ion and hydrogen bonds, CMC-PMAG and CMC-PHMG are stabilized by ionic, CMC-SNS hydrogen bonds, the correlation between which depends on the pH of the preparation and testing media [73] and determines the physico-mechanical properties. This circumstance is of great practical importance, because when using IPC in medicine, agriculture and water management, the pH can vary widely.

Since the IPC film is formed directly on the soil and in the body from a solution of a certain pH, the pH of the systems under study can influence the pH of the solution and, accordingly, the resulting film will have other physico-mechanical properties than the predetermined.

The dependence of the strength properties of IPC and CMC films in the air-dry state on the conditions for their preparation (pH of the solution) is shown in Fig. 2.29. When the pH of the solution decreases, i.e. when the acidity of the medium decreases to pH = 2.5, the value of the rupture voltage increases for all films (cr.1-5). This is due to the fact that at high acidity of the medium, the CMC macromolecule is folded into a static coil [182, 183]. As the acidity of the solution decreases, the static coil loosens, while the heterogeneity of the system decreases, and the strength of the film increases, which is recorded by increasing its breakdown voltage (Fig. 2.29).

The highest values of strength properties are observed in IPC films obtained from solutions with pH = 2.5, since they are stabilized by the maximum number of interchain hydrogen and ionic bonds.

With a further increase in the pH of the solution (up to pH = 9), the number of interchain bonds decreases due to rupture of the interchain hydrogen bonds, which leads to a decrease in the rupture stress of the IPC films (Fig. 2.29, cr.1,5).



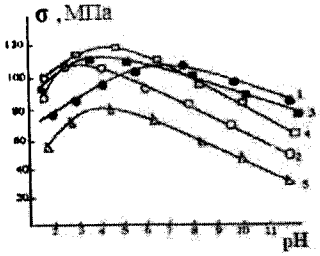



*Fig. 2.29. Dependence of the rupture voltage y for IPC films in the air-dry state from the conditions of their production (pH medium). Measurement temperature 298 K. 1 - CMC; 2 - IPC CMC-UFR; 3 - IPC CMC-PMAG; 4 - IPC CMC-PHMG; 5 - IPC CMC-SNS.*

Thus, the IPC film obtained from the solution with pH = 2-3 has the highest strength properties.

In conclusion, it can be said that the conducted studies make it possible to ascertain a relationship between the type and number of interchain bonds and the structure and properties of the final products, the films. The more ionic bonds, the greater the absolute strength of the IPC film. The greatest value of strength properties are films of equimolar composition CMC-PHMG, obtained from a solution with pH = 3+5.

The formation of heterogeneous structures in the IPC system leads to an unequal distribution of the load and lowers the strength properties of the films. The least heterogeneity of the system, and therefore the greatest strength, is achieved in the film with an equimolar component ratio.

## 2.7. Study of the thermal stability of interpolymer complex films

Studies of the thermal transformation of interpolymer complexes are of great interest, since the features of this process are directly related to the structure of the polymer body. In practical terms, these studies are relevant in that they make it possible to determine the temperature range of operation of IPC films, which, among other things, can be used at high temperatures. Scientifically, such studies are of independent value, since thermal properties are one of the important characteristics of polymer materials.

It is known that interpolymer complexes are formed from polymers having reactive functional groups and their heating leads to the formation

of interchain covalent bonds, both in PEC [14,184] and in PC [185]. The kinetics of the formation of amide bonds was studied in [14, 184] using the PAA-PEI system as an example and the step-by-step flow of the amidation reaction was shown, which depends on the structural complementarity of the initial polymer reagents.

The study of thermochemical reactions in polycomplexes of PAA and UFR has shown the possibility of increasing the thermal stability of polymers based on urea-formaldehyde resins [185-187]. The considered thermochemical reaction leading to the formation of a new polymer material with a significant change in mechanical and filtration properties, as well as swelling in aqueous and salt media, is one of the ways of chemical modification of IPC.

Such an approach to the modification of polymeric materials was used to obtain cross-linked hydrogels of the PAA-PEI polyelectrolyte complex. I.V. Zheleznova [159] showed that by varying the nature and quantity of stabilizing gel bonds (salt, covalent, hydrogen), it is possible to vary the properties of hydrogels from PEC in a wide range.

The results of thermal analysis of CMC, UFR, IPC films and their mechanical mixture are shown in Fig. 2.30. Endo-effects in the temperature range 368-339 K are associated with the removal of sorbed water. The exothermic effect at 563 K, associated with the oxidative thermal destruction of the polymer, appears on the CMC derivatogram (Fig. 2.30, cr. 1), and the total mass loss in the temperature range 323-773 K is 70-75%. Derivatogramm UFR (Fig.2.30, cr.2) is characterized by an exo-effect at 643 K. The decomposition of UFR begins at 503 K, and is associated with the breakage of amide bonds in urea fragments [61]. The total mass loss of the sample is 80% in the range 323-773 K. The IPC thermogram (Fig. 2.30, cr. 3) is characterized by the presence of a stretched exothermic effect with a maximum at 578 K. The weight loss in the sample at 323-773 K is 63%. Derivatograms of mechanical mixtures CMC-UFR (Fig.2.30, cr.4) show endo-and exo-effects, characteristic for individual components. In Fig.2.30, cr.4, the dots calculated from curves 1 and 2 of Fig. 2.30 (with the independence of the transformations in CMC and UFR) are indicated by the points for the mechanical mixture of CMC-UFR of equimolar composition (calculation by the formula $Ш_{см}=(Ш_{CMC}+Ш_{UFR})/2$) [33], which agrees well with the experimental data, indicating that the thermal destruction process proceeds independently in a mechanical CMC-UFR mixture.

Thus, the study of the thermal effect on the materials studied showed that the nature of the processes occurring during their heating is different for IPC, individual polymer components (CMC and UFR), and their



[redacted] mixture. Namely, the thermal stability of the IPC is higher than [redacted] of the individual components and their mechanical mixture, which is a [redacted] of the formation of interchain bonds between CMC and UFR.

From the curves in Fig. 2.31, it can be seen that the IPC sample has a [redacted] thermal stability than the UFR. Thus, at a linear heating rate of 10 [redacted] min, a 50% mass loss in UFR is observed at 563 K, whereas in the [redacted] this occurs at 588 K [185].

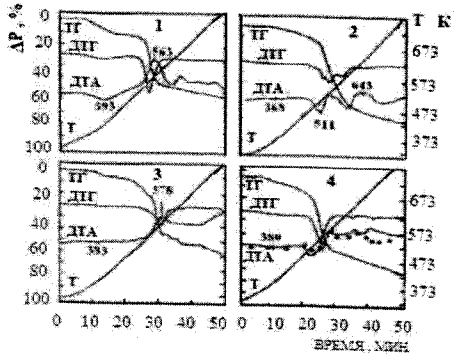



*Fig.2.30. Derivatograms: 1-CMC; 2-UFR; 3-IPC CMC:UFR = 3:2, obtained at pH = 2.5, 4 - mechanical mixture of CMC with UFR equimolar composition. The reference is calcined alumina ($Al_2O_3$).*

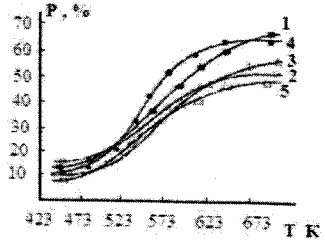



*Fig.2.31. Thermogravimetric curves of CMC (5);UFR, (4) and IPC:1 - CMC-$UFR_1$; 2 - CMC-$UFR_2$; 3 - CMC-$UFR_3$*

To determine the nature of the interaction between CMC and UFR, and their thermal stability, urea-formaldehyde oligomers ($UFR_1$, $UFR_2$ and $UFR_3$) obtained under laboratory conditions, a cyclic chain structure, containing a different number of triazinonic fragments ($UFR_1$-7%, $UFR_2$-15% and $UFR_3$ - 35%).

The endoeffect at 386 K, 391 K, and 383 K is associated with the

removal of sorbed water, respectively, and the minimum at 503 K, 498 K, 513 K refers to the isolation of reaction water on the derivatives of CMC-$UFR_1$, CMC-$UFR_2$ and CMC-$UFR_3$. This leads to an intensive formation of covalent bonds. Thermograms CMC-$UFR_1$, CMC-$UFR_2$ and CMC-$UFR_3$ are characterized by the presence of a wide exothermic effect with maxima of 591-650, 588-638, 573-608 K, respectively, which indicates the occurrence of oxidative thermal destruction processes leading to decarboxylation of IPC. The total mass loss of CMC-$UFR_1$, CMC-$UFR_2$ and CMC-$UFR_3$ samples in the temperature range 323-773 K is 74.59, and 62%, respectively (Fig. 2.31). The integral dependence of the mass loss of the IPC on temperature shows that the CMC-$UFR_1$ sample has a greater thermal stability than the CMC-$UFR_2$, CMC-$UFR_3$ in the temperature range of 573 K. For example, at a linear heating rate of 10 deg / min, a 50% in CMC-UFR2 is observed at 581 K, and in CMC-$UFR_3$ at 568 K, while at CMC-UFR, this occurs at 588 K. Consequently, an increase in the number of triazinone ring fragments in the UFR chain affects the nature, structure IPC, manifested in increasing the degree of loosening of the system, which leads to a certain decrease in the thermal stability of the films.

The process of formation of new interpolymer covalent bonds is manifested in the corresponding changes in the IR spectra of IPC films subjected to heat treatment in the temperature range 373-623 K.

Figure 2.32 shows the IR spectra of the initial IPC of CMC-UFR, (cr1) and polycomplexes (cr.2-5), subjected to heating at temperatures in the range 373-623 K for 30 minutes. It can be seen that as the temperature rises from 373 to 553 K, the intensity of the absorption bands decreases at 1585 $cm^{-1}$ (asymmetric vibrations -COO-groups) and at 1420 $cm^{-1}$ (symmetrical vibrations-COO groups). In the reaction for the formation of amide bonds, only those functional groups of macromolecules that formed ionic bonds in the initial IPC participate [14,144]. Carboxyl groups located in the defective areas of IPC do not participate in the reaction when the samples are heated to 403 K, which is indicated by the constancy of the intensity of the absorption bands at 1720 $cm^{-1}$, related to the stretching vibrations of the non-ionized carboxyl group (Fig. 2.32). Obviously, when heated, the protonated COOH groups in the defective parts of the IPC enter the anhydride formation reaction, which follows from the displacement of the absorption bands at 1740 $cm^{-1}$ at a temperature of 553 K, 573 K (Fig. 2.32).



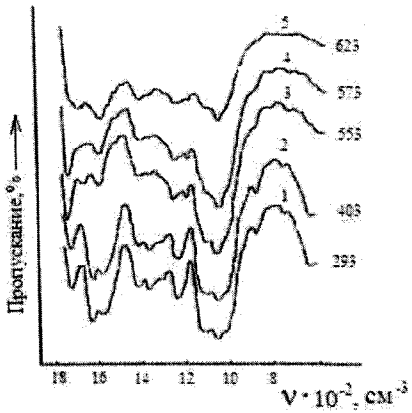
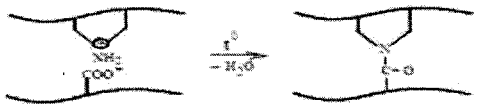



*Fig.2.32. IR spectra of films of the interpolymer complex CMC-$UFR_1$, heated at various temperatures for 30 min.*

A further increase in the temperature of heating of IPC films to 623 K leads to oxidative thermal destruction of IPC and complete dehydration and decarboxylation takes place. In the IR spectra, the absorption bands disappear at 1720 $cm^{-1}$ (asymmetric vibrations-COO groups). The above changes in the IR spectra of the CMC-UFR are in good agreement with the data obtained by thermogravimetry, the structural changes of which can be represented by the following scheme:




(2.20)

To study the solubility of heat-treated IPC, IPC films were obtained from solutions with pH = 6-8 with an equimolar ratio of the components. The films were held for 30 minutes. at various temperatures (323-523 K), and then their solubility by the weight method was investigated on a microanalytic balance. The weighed samples were placed in bucks and filled with distilled water, held at 298 K for 24 hours, and the weight of the insoluble part of the IPC mixture was determined.

Starting with the heat treatment temperature of 393 K (Fig. 2.33), the solubility of all films decreases. Films IPC CMC-$UFR_2$ and CMC-$UFR_3$,

subjected to heat treatment at 473 K, completely lose the ability to dissolve in water, while the similarly treated CMC-$UFR_1$ film still partially retains the ability to dissolve (by 40%). These facts can be explained by the fact that the thermal treatment of films leads to a change in the nature of the interchain bonds-the conversion of salt bonds to amide bonds [184,188]

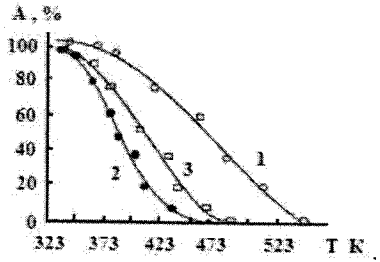



*Fig.2.33. Dependence of the solubility (A,%) of heat-treated IPC films (equimolar ratios obtained in a neutral medium) on the processing temperature 1 - CMC-$UFR_1$; 2 - CMC-$UFR_2$; 3 - CMC-$UFR_3$.*

In films of composition CMC-$UFR_2$ and CMC-$UFR_3$, the concentration of interchain ion bonds (> 15%) is higher than in the CMC-$UFR_1$ film (7%). The higher the concentration of ionic bonds in the initial films, the higher the amount of amide bonds formed, respectively. The more amide bonds there are, the lower the film solubility [184,188]. Indeed, the solubility of the heat-treated films CMC-$UFR_2$ and CMC-$UFR_3$ (Fig. 2.33, cr. 2.3), as was already mentioned, is lower than the solubility of the CMC-$UFR_1$ film (cr. 1).

It was shown in the paper [189] that 10% of the intermolecular amide bonds are sufficient to ensure the integrity of the IPC films. Obviously, this explains almost the same solubility of heat-treated films CMC-$UFR_2$ and CMC-$UFR_3$ (Fig. 2.33, cr. 2.3) containing > 15% intermolecular bonds.

Thus, the fact of loss of solubility by IPC films containing > 15% of interchain ion bonds after their heat treatment at 200 °C confirms the assumption that under the influence of temperature in the films of the interpolymer complex an irreversible change in the intermolecular interaction takes place-ionic bonds transfer in amide. This agrees with the data obtained by us for differential thermal analysis, IR-spectroscopy, swelling, and literature data [184].



# CHAPTER 3. INTERPOLYMER COMPLEXES IN MEDICINE

## 3. 1. Interpolymer complexes for pharmacology

The way in which polymers are used in medicine is related to the idea of prolonging the effect of drugs if they are suspended by their molecules to side groups to the polymer chain, which is "neutral" to the body. This idea was implemented in the early 1950s.

The original idea was quite simple: the low efficiency of low-molecular drugs is due to the fact that they are too quickly carried away by the blood flow; if they manage to stop them in the body, the effectiveness will increase dramatically. In the first experiments polyvinyl alcohol was chosen as the neutral carrier.

Despite the relatively short period of intensive research of interpolymer complexes (IPC), the uniqueness and originality of their properties determined the closest attention to the practical use of polymer materials based on them.

Promising, from the point of view of application as biomedical materials, are IPC based on chitosan [190-192]. Water-insoluble films of this IPC proved to be effective as an artificial skin for accelerating the healing of wounds with large burn lesions. Films made from IPC based on chitosan are usually obtained in three to four component mixtures of solvents, they have high strength, permeability and good moisture absorption [190]. High biocompatibility with tissues of living organisms allows using them as membranes and microcapsules for immobilization of enzymes, biologically active cells and microorganisms [192, 193].

Valuable properties of IPC based on chitosan are: their high adhesion strength, which allowed them to be used in the treatment of the oral cavity and periodontal diseases [194].

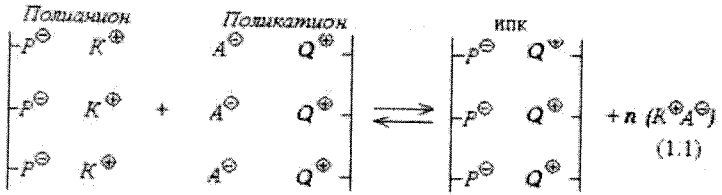
IPC are very promising materials for use as tissue substitutes in the body [142]. However, often films or hydrogels of IPCs do not have sufficient mechanical strength for their practical use as structural materials.

The development of endogenous prosthetics in cardiovascular surgery [195], the extensive clinical use of extracorporeal circulation [196], the achievements in the technique of blood separation into components [197], the development of implantable systems with dispensed drug release [198] are largely determined by the successes of chemistry and technology of polymers of medical purpose [199]. Among the diverse requirements for such polymers, there is a general and essential requirement: medical supplies must be biocompatible or hemocompatible if they are supposed to be in direct contact with blood. Research into the development of polymeric materials for medical purposes has recently led to the solution of

a number of important practical problems. Thus, the atrium and ventricles of the artificial heart, coatings for prostheses of blood vessels, coatings for carbon hemosorbents, etc. have been created.

When considering the medico-biological properties of IPC, the authors of the paper [200] discussed mainly the problems of thrombus formation in the contact of blood with IPC. The formation of a blood clot upon contact of blood with a foreign surface is a natural reaction of any living organism. At the same time, this process is the greatest danger when implanting various materials. Obviously, hemocompatible material should not, in the first instance, cause vigorous thrombus formation when it is brought into contact with blood, i.e., it must be thrombus resistant [200].

The development of specific methods and processes for obtaining products from IPC is based on reaction control (3.1):



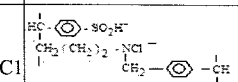
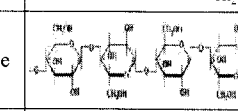
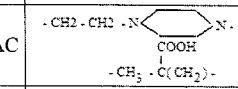
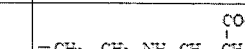
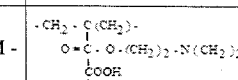
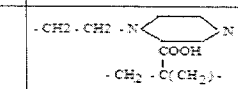

where $K^+$ and $A^-$ are low molecular weight cations and anions.

As follows from the equation of this reaction, the introduction of excess quantities of low-molecular electrolytes (salts, acids, alkalis) into the system leads to a shift of equilibrium to the left. Thus, the initial solutions of non-interacting polyelectrolytes are obtained. In turn, the processing of the initial solutions is based on techniques that allow the equilibrium of the reaction (3.1) to shift toward the formation of IPC by decreasing the activity of low-molecular electrolytes. In this case, the phase separation of the system takes place and the reaction product (3.1) - IPC - is released in the form of a hydrogel. In practice this process is carried out by sharp dilution of the system with water [7-9] or by evaporation of a volatile low-molecular-weight electrolyte [73,158,201]. These methods were widely used in the production of coatings of elements and parts of the artificial heart, vascular prostheses, semipermeable membranes, coatings on hemosorbents, etc. [72,202,203]. In these studies, a variety of IPCs were used, among which IPC's, formed by weak polyelectrolytes - polymer carboxylic acids and polymeric amines, occupy an important place (Table 3.1). The physicochemical processes taking place in the formation of hydrogels of IPC are discussed in detail in [7,12-14,57,73,158].



Table 3.1.

**Components of IPC studied as thrombo-resistant materials**

| Name of IPC | Notation | Link Formulas | A source literature |
|---|---|---|---|
| Polystyrene sulfonate - poly (vinyl benzyltrimethylammonium) chloride | PSS-PVBTMACl |  | [202-204] |
| Heparin-2,5-ionene-bromide | Hep-ionene |  | [205] |
| Polyethylenepiperazine-polyacrylic acid | PEPP - PAC |  | [96, 206] |
| Polyethylenimine-polyacrylic acid | PEI-PAC |  | [206, 207] |
| Polydimethyl-aminoethyl methacrylate is polyacrylic acid | PDMAEM - PAC |  | [96, 206] |
| Polyethylene piperazine polymethacrylic acid | PEPP-PMAC |  | [96, 206] |

The ability of PEC to swell is due to the structural features of these interpolymer compounds. The degree of swelling can be controlled over a wide range, changing the ratio of the links included in the relatively hydrophobic and hydrophilic portions of the IPC. This, in turn, can be achieved either by shifting the equilibrium of reaction (3.1), or by changing the composition of PEC [8,158,203]. Swelling of IPC is one of the most important properties that determine the possibility of using these systems for medical purposes. IPC is also characterized by high permeability for water, substances dissolved in water and gases. The experimental results given in Table 3.2, indicate that the transport characteristics of the IPC hydrogels are close to those for the best of the modern hydrate-cellulose membranes used in medicine [73, 74].

Table 3.2.

**Transport characteristics of IPC**

| IPC | Degree of swelling, g H2O /g of polymer | Coefficient permeability, cm | Dialysis permeability constant for urea, cm/min | Dialysis permeability constant for vitamin B 12, cm/min |
|---|---|---|---|---|
| PEPP- PACK | 1,04 | $2{,}35\text{-}10^{-14}$ | $20\text{-}10^{-3}$ | $1{,}4\text{-}10^{-3}$ |
| PEI- PACK | 0,7 | $1{,}7\text{-}10^{-14}$ | $19\text{-}10^{-3}$ | - |
| Film 100 | 0,69 | $0{,}95*10^{-15}$ | $21*10^{-3}$ | $1{,}4\text{-}10^{-3}$ |
| Cuprophan | 1,7 | $0{,}503*10^{-15}$ | $44\text{-}10^{-3}$ | $5{,}8*10^{-3}$ |
| Diacelli | 1,4 | $0{,}2\text{-}10^{-14}$ | $41\text{-}10^{-3}$ | $6{,}0\text{-}10^{-3}$ |

Along with the high permeability of IPC relatively low-molecular substances, these systems are practically impenetrable for proteins and even more so for blood cells [73,203]. An important feature of the diffusion permeability of IPC hydrogels is their selectivity with respect to charged particles [38]. Reduced permeability of membranes from IPC for: $Cl^-$, $Na^+$, ions, as well as lysine, glutamine, phenylalanine and others is associated with the presence in the IPC structure of regions with separated ionogenic groups forming charged loops.

Possibilities of practical use of hydrogels IPC in medicine are largely determined by the complex of their physico-mechanical properties. For IPC, which are in an equilibrium swollen state, large irreversible deformations are characteristic for relatively low voltages. Figure 3.1 shows the typical deformation-strength IPC curves resembling similar curves for elastomers [73,202,203].

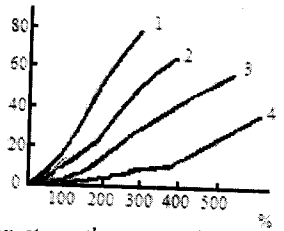



*Fig. 3.1. Deformation-strength curves of the stoichiometric gel of the IPC PEPP-PAC at various temperatures. On the abscissa axis, the strain (in%), along the ordinate axis, the stress (in kg / cm$^2$). 1-283 K: 2-293 K; 3-303 K; 4-313 K.*



Obviously, the low strength properties of the IPC hydrogels limit the ability of their use, but at the present time approaches are being developed that improve the complex of physico-mechanical properties of IPC. First of all, this is a chemical modification of the IPC, which consists in the partial replacement of salt interpolymer bonds by covalent bonds [81]. Perspective is also the creation of composite materials based on IPC, for example, mixtures with elastomers and plastics by combining IPC with the corresponding latexes [81,82].

The considered properties of the hydrogels of IPC open wide possibilities for their application in various fields of medicine as semipermeable separation membranes, biocompatible coatings, dosage delivery systems, etc. In those cases when the direct contact of the material with the tissues of a living organism is assumed, biocompatibility plays a decisive role. In the proposed work, materials based on IPC for direct contact with blood are mainly considered. In this regard, the nature of the Hemocompatibility of IPC is discussed and, as one of its most important aspects – thrombus resistance.

### 3.2. Thrombus resistant properties of IPC

The thrombus resistant properties of materials can be reliably judged only on the basis of complexes of testing methods *in vivo*, *ex vivo*, *in vitro* [96,205,208]. To date, numerous data from medical and biological experiments have been accumulated for a wide range of IPC [96,203-205].

**Study of thrombus resistant properties of IPC in "in vivo" experiments.** The study of the *in vivo* behavior of polymeric materials intended for direct contact with blood is the final and necessary stage of testing, which opens the way to medical practice [96, 208]. In such experiments, performed with the participation of the authors of the article [204,207,208-210], polymeric medical products were studied: thrombotic traps, catheters, artificial heart, vascular prostheses, hemosorbents, on the surface of which were applied IPC. Acute and chronic experiments were performed on dogs and calves in conditions of constant blood flow [208,209].

Analysis of the results of these experiments showed that prosthetics as the main (abdominal aorta) and peripheral (iliac arteries) blood vessels within a period of 1 day up to 14 months is not accompanied by thrombosis (Table 3.3). In experiments on complete replacement of the abdominal aorta and iliac arteries, where a large enough contact of blood with the polymer surface is carried out, in prostheses of vessels coated with IPC for 14 months thrombus formation was not observed. At the same time, the

results of control experiments on alloplasty of the iliac arteries and aor with standard fluorenolaurasan prostheses showed that for them the numb of cases of thrombus formation is 75%. Experiments on animals were al performed with iliac veins, where the blood flow velocity is lower and consequently, the tendency to thrombus formation is higher. The thrombu was absent at terms up to 2 days on IPC-covered shunts, whereas fo uncovered shunts, thrombosis occurred 2-3 hours later [200].

Table 3.3.

**Thrombus resistant properties of prosthetic vessels and devices, coated with IPC PAC - PEPP implanted in the vascular bed**

| Experiment name | Type of animal | Number of observations | Term of Observations | Availability of Thrombus |
|---|---|---|---|---|
| Alloplasty of the abdominal aorta with lavsan prostheses covered with the IPC PAC-PEPP (z = l) | Dogs | 1<br>2<br>2<br>2<br>2<br>2<br>1<br>1<br>1<br>1<br>1<br>1 | 1day<br>2 days<br>3 days<br>4 days<br>5 days<br>6 days<br>7 days<br>15 months<br>2,5 months<br>3,5 months<br>4,5 months<br>6 months<br>14 months | No-*II*-<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-*<br>*-II-* |
| | | Total 17 | | |
| Alloplasty of the iliac artery by prostheses based on lavsan coated with IPC PAC-PEPP (z = 1) | Dogs | 2<br>1<br>1<br>1<br>1 | 7 days<br>15 days<br>2,5 months<br>3.5 months<br>6 months | *No Thrombus filled 2/3 prosth esis No -II- -II -* |
| | | Total 6 | | |
| Complete replacement of the abdominal aorta and iliac arteries with lavsan prostheses coated with IPC on the basis of PAC-PEPP (z = 0.66) | Dogs | 1 | 14 months | No |



| | | | | |
|---|---|---|---|---|
| [redacted] shunt between [redacted] artery and the [redacted] vein of organosilicone [redacted] coated with IPC PAC-PEPP (z = 0.66) | dogs | 1 | 14 months | No |
| [redacted] of connecting [redacted] during orthotopic [redacted] of an artificial heart [redacted] on lavsan and silicone [redacted] coated with IPC PAC-PEPP (z = 0.66) | Calves | 2<br>3 | 8 hours<br>10 hours | No |
| [redacted] into the ileum-[redacted] vessel call of umbrella [redacted] filters based on silicone [redacted] coated with IPC-PETP (z = 0.64) | Dogs | 6 | 6 months | No |
| [redacted] of the abdominal [redacted] with lavsan prostheses (control) | Dogs | 3 | 1.5 months | Thrombus in 2 cases |
| [redacted] of the iliac artery with lavsan dentures (control) | Dogs | 1 | 15 days | Thrombus |
| Implantation of connecting trunks during orthotopic implantation of an artificial heart based on lavsan and silicone rubber (control ) | Calves | 7 | 10 hours | Availability of wall blood clots |
| An arteriovenous shunt between the carotic artery and the jugularis vein of silicone rubber (control ) | Dogs | 1 | 2.5 hours | Thrombus |

In experiments on calves for implantation of connecting trunks coated with IPC during orthotopic implantation of an artificial heart, a thrombus was not seen within 10 hours, while numerous thrombi were observed in the cavities of the artificial Heart made from PDMC. In the trunks not

covered by IPC, at the same time (control experiments) thrombotic formations were also observed [200].

The results of macro- and microscopic studies of implants of polymer structures coated with IPC show that IPC does not cause reactive inflammation of natural tissues, surrounding the implant, and promote the regeneration of endothelium and connective tissue. Examination of long-term implant in blood flow conditions with IPC coatings indicates that the main hemocoagulant indices are already normalized during the early postoperative period, which also indicates a high thrombolytic resistance of IPC.

Thus, it can be argued that IPC, formed by different pairs of polyelectrolytes, has a high thrombolytic resistance, i.e., this property is inherent in the whole class of these interpolymer compounds.

However, *in vivo* experiments do not allow us to reveal the details of processes occurring at the polymer-blood interface, and thereby ascertain correlations between the structure and the physicochemical properties of the materials, on the one hand, and the state of the coagulation system of blood on the other. To a certain extent, these problems can be solved by performing experiments **"ex vivo".**

**The results of the "ex vivo" experiments.** Experiments *ex vivo* allow you to detail the effect of different materials on individual stages of the thrombus formation process without a significant disruption of hemostasis. The results of *ex vivo* experiments under conditions of hemosorption on carbon hemosorbents of the SKN and GS-01 brands [209,211] with IPC coatings are considered below [207].

The study of the interaction of blood with coatings from IPC PEI-PAC and 2,5-ionene-heparin was performed under conditions of hemoperfusion on dogs. Special attention was paid to the interaction of platelets with sorbents. As follows from Fig. 3.2, for sorbents without coverage, there is a significant decrease in the number of platelets in the total blood stream, while for coated IPC sorbents only in the first 10 min. perfusion, there was a slight decrease in the concentration of platelets, the number of which was subsequently restored to the original level. This indicates a practical lack of adhesion of platelets to coatings from the IPC.



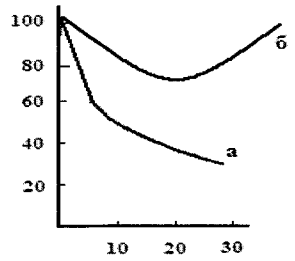



*Fig.3.2. Dynamics of changes in platelet concentration in the total blood flow during hemosorption.*
*The abscissa is the time (in minutes); ordinate - the content of platelets in 1 cm3 of blood (in% of the initial level), and - uncoated sorbent; b - sorbent coated with IPC.*

In addition, there is a significant difference in the morphology of the platelets that come into contact with the surface of the carbon hemosorbent, and the sorbent, protected by the coating from the IPC. The surface of the carbon sorbent is covered by a significant number of severely deformed platelets, platelet aggregates and fibrin filaments. At the same time, rare platelets that are trapped on the surface protected by IPC are not subjected to significant morphological changes and do not aggregate [200].

In special experiments, it was shown [210] that as a result of the contact of blood with a carbon sorbent, the activity of most coagulation factors decreases. Especially noticeably decreases the activity of VII, IX and XII factors and, on the contrary, increases the activity of factor VIII, which, in combination with Villebrand factor, is responsible for platelet aggregation. The protective coating from the IPC PEI-PAC significantly reduces the disruption of the activity of the same factors, and a coating based on 2,5-ionene-heparin practically does not lead to their changes. This indicates that there is no appreciable interaction of plasma proteins with IPC.

Further development of ideas about the nature and mechanism of the interaction of the most important components of blood with hydrogels of IPC can be obtained in the model conditions in **"in vitro"** experiments.

**The results of the experiments "in vitro.** Almost all of the data given in Table 3.1 systems were studied in the **in vitro** conditions. Such experiments were carried out with films and coatings from IPC, using both whole and stabilized blood [200].

Let us consider the interaction of IPC with proteins at different stages of the blood coagulation process using the example of IPC PEPP-PAC and

PEPP-PEI-PAC of various compositions z, (z = [PEPP] / [PAC] base-mole / base-mole). It follows from Fig.3.3 that the sorption of plasma proteins by IPC films is more than 2 times lower in comparison with the control sample from PMMA [206].

The data in Table 3.4 indicate a decrease in sorption of the most important protein of the fibrinogen blood coagulation system by PEPP-PPA polycomplexes of different composition as compared to polyethylene and glass (control).

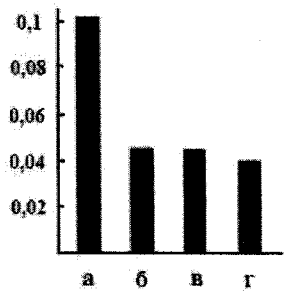



*Fig.3.3. Sorption of the total protein of plasma IPC.*

*The abscissa is z; on the ordinate axis - the amount of sorbed protein (in mg / cm2). a - PMMA; b-PEPP-PAC z = 1; c - PEPP-PAC z = 0.05; g - PEPP PAC z = 0.33.*

Table 3.4.

**Sorption of fibrinogen by various surfaces**

| Material | The amount of fibrinogen, mg% |
|---|---|
| Glass | 380±20 |
| PE | 280±30 |
| PE with grafting PAC | 260±30 |
| IPC z = 1, deposited on PE | 180±20 |
| IPC z = 0.5, deposited on PE | 150±10 |
| IPC z = 0.33, deposited on PE | 200±30 |

When studying the behavior of hydrogels of different IPCs in whole and stabilized blood, as well as thrombocytopenic plasma, a significant decrease in the relative platelet adhesion index and a corresponding



increase in clotting time were found, compared with the values for control materials. From the data presented in Fig.3.4, it follows that adhesion of platelets with hydrogels of IPC of different composition is poorly expressed, and this is most clearly manifested for IPC PEPP-PAC enriched with negatively charged ion electrolyte (PAC). IPC also does not have a traumatic effect on other blood elements, such as red blood cells. Hemolysis in contact with hydrogels of IPC does not exceed the natural level [200].

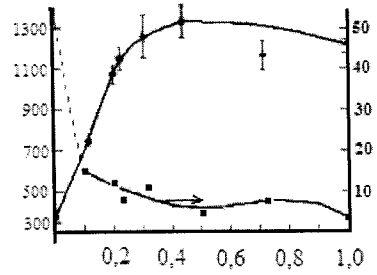



*Fig.3.4. Blood coagulation time in the Lindholm chamber (dark circles) and platelet adhesion index in Murphy's chamber (dark squares) for IPC PEPP-PAC different composition (0.1 <z <1) compared to glass.*

*The abscissa is z; on the ordinate axis: on the left - the time of blood coagulation (in sec), on the right - the platelet adhesion index.*

To evaluate the functional properties of thrombocytes, the authors of the paper [200] used electron microscopy. Figure 3.5, (b) presents an electron microscopic photograph of the surface of polyethylene (PE) after contacting it with blood, on which it is possible to distinguish both individual platelets and their aggregates. A similar picture is also observed on the microphotography of the surface of PE with grafted PAA after its contact with blood. If, in the blood, the samples of IPC PEPP-PAC or PE films coated with the same IPC are swollen in phosphate buffer, then in electron microscopic studies of such samples, platelets in the field of vision practically are not detected (Fig.3.5, b). Similar results were obtained in work [212] for IPC of another chemical nature.

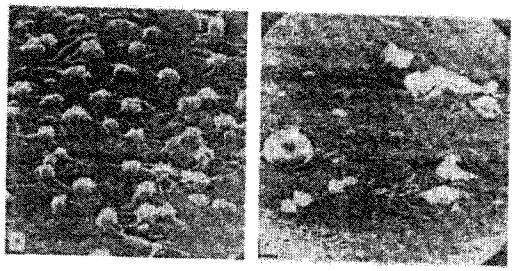


*Fig.3.5. Electron micrograph of the surface of polyethylene after contact with blood (a) and the surface of the IPC PEPP-PAC film (z-0.5) after contact with blood (b).*

Thus, as a result of numerous studies performed for different IPC pairs, it has been ascertained that IPC are thrombus resistant materials [202,203,205,212,213].

Since thrombus resistance is inherent in a wide range of polymeric compounds - IPC, it is possible to ascertain correlations between the structure, physicochemical properties and medical and biological characteristics of these promising materials. The detection of such correlations is necessary for the directed synthesis of polycomplex systems with the necessary medical and biological properties.

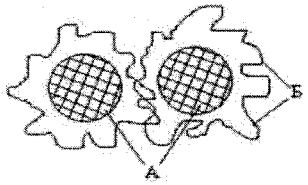
### 3.3. The concept of thrombolytic resistance of IPC

IPC structures and experimental data on the hemocompatibility of these interpolymer compounds allow us to make a general conclusion about the nature of thrombus resistance of IPC. Essential here are the following provisions: a) the presence of an irregular structure formed by different pairs of polyelectrolytes formed by different pairs of polyelectrolytes, defect sites - loops [7,10,12]: (b) a small affinity of the IPC for blood proteins [96,205, 207, 212].

The first provision is crucial for understanding the nature of the interaction of the IPC or, what is the same, the various surfaces modified by the IPC, with the shaped elements of the blood. Naturally, the greatest interest is the interaction of IPC with thrombocytes responsible for the state of the coagulating system of blood. It should be noted that the linear dimensions of these blood cells (~ 2 μm) correspond to the sizes of typical colloidal particles. If we assume that biochemical changes in platelets leading to the organization of a platelet thrombus start only after contact



with an alien surface, then at the stage of primary interaction of blood platelets with the surface they can be considered as colloidal particles. Within the framework of such representations, the interaction of platelets with phase interfaces can be assessed from the positions taken in colloid chemistry.



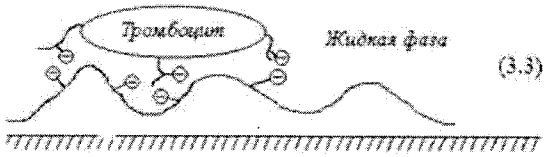
(3.2)

It is known that by the adsorption of a polymer on the surface of colloidal particles, stability of the colloidal system can be substantially enhanced. The nature of such steric stabilization of colloidal systems becomes understandable when considering scheme 3.2 [200].

Scheme 3.2 shows 2 colloidal particles with macromolecules adsorbed on the surface, some of whose links are connected to the particle surface and assembled in the sequence (A). Other links are included in the "loops" and "tails" (B). If the extent (number) of links included in the "loops" and "tails" is not too small, then when repelling such particles with each other, repulsive forces arise. The appearance of such forces is due to a decrease in the volume in which the links of the "loops" and "tails" are distributed as the particles approach each other.

In other words, repulsion is caused by an increase in the osmotic pressure in the region of chain overlap due to an increase in the concentration of their segments as the particles approach the surface [214,215].

Obviously, this approach remains valid for the case when the interaction of a colloid particle with a flat surface on which a polymer is adsorbed is involved. It is this situation that arises when the surface of the IPC and platelet interacts (Scheme 3.3) [200].

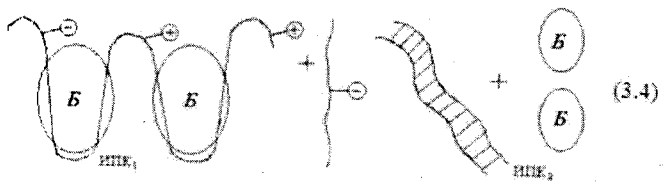



(3.3)

The role of "loops" and "tails" of macromolecules facing the liqui phase (blood plasma, physiological solution) is played by defects in th structure of the IPC. For the stoichiometric composition or enriched PAC studied by the IPC, these sites are formed by negatively charged PAC unit carrying the COO group. The "spherical" repulsion effect is achieved eve if only one of the components has a polymer chain on the "loop" and "tail" surface, in this case the IPC. However, it is known that rather extensive segments of polysaccharide chains facing outward are embedded in the platelet membrane. They are part of the envelope surrounding the membrane of the cell [76] and also contribute to the repulsion that occurs between the IPC surface and the platelet. This repulsion, as was shown above, is observed experimentally and manifests itself in a small adhesion of platelets to surfaces covered with IPC. It is also manifested in the absence of morphological changes in thrombocytes that settle on such surfaces by the action of gravity, while platelets on the surface of the IPC retain their characteristic shape and do not spread out.

Reduced adsorption of blood plasma proteins, including fibrinogen, on the IPC surface can also be explained on the basis of the peculiarities of the IPC structure.

At the present time, the interaction of blood plasma proteins with polyelectrolytes in solution has been fairly well studied [52,54,55,216]. Without going into detail in the discussion of these studies, we note that polyampholyte proteins are very prone to the formation of stable compounds with synthetic polyelectrolytes of different charge sign; these compounds are of the IPC type [54,55,216]. It is essential that synthetic polyelectrolytes effectively replace plasma proteins from such IPCs by reaction (3.1) according to scheme 3.4. In this reaction, the IPC protein-polyelectrolyte and the polyelectrolyte of the opposite charge sign participate. The reaction products (scheme 3.4) are free protein (B) and IPC formed by two synthetic polyelectrolytes [52,54,216].




(3.4)



Thus, the protein is not a competitor in the reaction between electrolytes. Naturally, for the same reason, blood plasma proteins are able to bind with IPC particles, the latter would correspond to the [illegible] of the reaction (see Scheme 3.4) from right to left. The above [illegible] explain the experimentally observed low affinity of proteins for [illegible] surfaces coated with IPC [80,217].

The above explanation of the thrombotic resistance of IPC and various [illegible] covered by IPC is based on the lack of interaction between them [illegible] the most important components of the blood plasma, providing [illegible] formation (fibrinogen and platelets). The latter are even [illegible]ively excluded from the areas occupied by IPC. The explanation is [illegible] on the most general idea of the structure of these macromolecular [illegible]pounds, which is why the absence of pronounced thrombus formation [illegible] contact of stoichiometric and enriched polyanionic components of [illegible] with blood is their common property and does not depend on the [illegible] chemical structure of the IPC constituent polyelectrolytes [illegible],200,205,212,217].

Among the thrombus resistant systems discussed above, also systems [illegible]med as a result of reversible adsorption of heparin from the solution to [illegible]tively charged surfaces. Positive charge is created by preliminary [illegible]sorption onto such surfaces of either polymer cations or polymer cationic [illegible]factants [218,219]. In the first case, the interaction of such a surface [illegible] heparin is accompanied by the formation of IPC (for example, [illegible] molecular compounds, such as 2,5-ionene-heparin) [200].

It is noteworthy that the structure of IPC is in general similar to the [illegible]ture of segregated block copolymers, which include hydrophobic and hydrophilic blocks, for example block copolymers of polyurethanes and polyesters (hydrophobic components) and polyoxyethylene and polyoxypropylene (hydrophilic blocks). A material based on such copolymers, called "Biomer", is one of the best thrombus resistant materials [220-222]. At the same time, there is information in the literature that hydrophilic blocks in such systems should form loops facing the environment. This follows from the data of the conformational analysis given in paper [14].

In paper [223] demonstrated thrombus resistance of polymeric materials, on the surface of which various hydrophilic nonionic polymers are grafted. The explanation of thrombus resistance is given on the basis of the notion of the lack of binding of proteins to such surfaces. However, the author sees the reasons for the reduced affinity of serum proteins for such materials in a very low surface tension at the polymer-water interface. The sorption of proteins, and in this case, can be discussed in terms of the

approaches described in [200] if we consider graft chains as poorly adsorbed on the surface of the polymer being modified. In this case, the conformation of the grafted chains can be represented as segments of a chain connected to the surface of the carrier polymer, as well as "loops" and "tails" facing the aqueous phase.

The above-mentioned reasons for thrombus resistance result from a general physico-chemical approach to the description of the interaction of certain blood components with a vast class of new macromolecular compounds - IPC. Obviously, these representations can not be generalized and extended to other thrombus resistant polymer systems, with the exception of some types of segregated block copolymers. This is natural, since the process of thrombus formation in contact with the blood of foreign surfaces is extremely complex and represents a set of biochemical reactions. Therefore, for the creation of thrombus resistant materials, a large number of different techniques can be used that allow one to influence the various phases of this process. One of such methods was demonstrated in [224] using the example of a thrombus resistant material based on hydrogels, in the volume of which heparin is immobilized. In contrast to the IPC considered in paper [200], the principle of the action of hydrogels is based on their ability to effectively bind fibrin-monomer and thereby shift the polymerization-depolymerization equilibrium of fibrinogen" fibrin towards formation of a monomeric protein. Most importantly, hydrogels, when placed in contact with a white thrombus, lead to its lysis. Immobilized proteolytic enzymes act on the same principle.

The enumeration of such examples could be continued, but this is beyond the scope of this paper. With certainty, it can only be noted that the prescriptions proposed in the present work on thrombus resistance are apparently of a rather general nature.

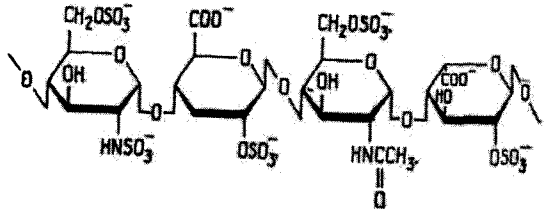
### 3.4. Depot model of an antiheparin preparation [225]

Widespread introduction to medical practice has received a new kind of detoxification of the body - hemosorption. Artificial blood flow, regardless of the purpose and design of perfusion systems, is possible only under the condition of reversible pharmacological reduction of blood coagulability. The condition of hypocoagulation provides a long flow of blood along the highways artificial systems, its interaction with the functional elements of the latter (with an oxygenator in the AIC sorbents during hemosorption, etc.).

Hypocoagulation of blood is achieved by injecting into the bloodstream a physiological anticoagulant of direct action-heparin (3.5),



which is a highly sulfated polysaccharide, possessing a strong negative charge due to the dissociation of carboxyl and sulfo groups.




(3.5)

The duration of anticoagulant effect of heparin with intra-vascular administration is proportional to its dose, but, as a rule, to the end of hemoperfusion it remains in the blood in sufficient quantity, and in order to avoid loss of blood from vessels damaged during surgery it should be neutralized. To this end, it is customary to introduce into the blood a heparin antagonist, which is a polymer cation of natural [226] or synthetic [227] origin. Their anti-heparin activity is a consequence of direct electrostatic interaction of multiple positive charges of antagonist molecules with negatively charged heparin. The product of this reaction is a low active and low-toxic interpolymer complex (**IPC**) [14]. However, high molecular weight heparin antagonists - polycations themselves can show high biological activity and toxicity due to their ability to interact cooperatively with proteins and cell membranes [228]. Therefore, an overdose of them is dangerous. In connection with this, the problem arises of precisely dosing the heparin antagonists when they are introduced into the blood. In the publications published so far, there is no satisfactory method for accurately determining heparin in the blood and calculating the neutralizing dose of the antagonist. The dangerous consequences of an overdose of the antagonist can be largely ruled out using the heparin antagonist depot. Such a depot can be, for example, a soluble **non-stoichiometric polyelectrolyte complex** (**NPEC**) formed by a synthetic polyanion and polycation, a heparin antagonist. Depot will be effective if heparin quantitatively binds its antagonist from NPEC, forming a new stoichiometric, physiologically inactive IPC, as shown in Fig. 3.6. The toxic heparin antagonist in the absence of the latter is always connected by an oppositely charged polymeric carrier. When heparin appears, the antagonist quantitatively binds to it, forming an insoluble physiologically inactive stoichiometric IPC.

Before considering the advantages of this approach and the process taking place in the system (see Fig. 3.6), it is necessary to briefly

characterize the original NPEC, which plays the role of heparin depot.

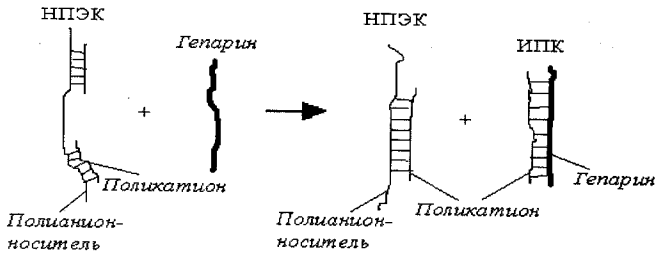



*Fig. 3.6. The depot of an antiheparin drug.*

As a model heparin antagonist, the authors of [225] used the **polycation-poly-4-vinylpyridinium bromide** (PVPB) available under laboratory conditions. The carrier of the antagonist was chosen a low-toxic polyanion - the **sodium salt of polymethacrylic acid** (PMA-Na), which forms in the physiological solution of NPEC with PVPB. The properties of such NPEC were described earlier [229]. Based on the well-known literature data, it can be asserted that NPECs are stable macromolecular compounds characterized by specific molecular weight, particle size, NPEC composition, etc. Speaking about the stability of NPEC, we mean that in physiological environments all the chains of PVPB are in a bound state, i.e., they are included in NPEC particles. In paper [225], NPECs having the index p = [PVPB] / [PMA-Na] = 0.33 and 0.2 (in square brackets the concentrations of units of oppositely charged polyelectrolytes included in the NPEC) are used. Table 3.5 describes the characteristics of polyelectrolytes forming NPEC, and the NPEC itself. According to modern ideas, the particles of such NPEC can be considered as a kind of block copolymer consisting of alternating single-stack blocks, which are a salt of PVPB and PMA-Na. The NPEC particle can be schematically depicted, as shown in Fig. 3.7. Such a particle is retained in the solution due to the presence of hydrophilic charged PMA-Na units, included in it in an excessive amount. It is these NPEC particles that appear on the left side of the diagram in Fig. 3.6 as the depot of the heparin antagonist.



Table 3.5.

**Characteristics of polyelectrolytes and polycomplexes**

| Polymer | Molecular weight (Mw) | The sedimentation coefficient, according to Svedberg | Molecules amount | |
|---|---|---|---|---|
| | | | PMA- | PMA- |
| NPEC | 1 326 000 | 5,2 | 4 | 24 |
| NPEC | | 5,5 | 3 | 18 |
| PMA | 64 000 | 2,8 | - | - |
| PVPB | 80 000 | 1,7 | - | - |

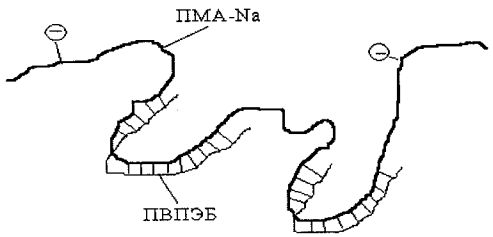



*Fig.3.7. Schematic representation of the NPEC particle.*

Additional evidence of the strength of the interaction of pairs of oppositely charged polyelectrolytes in NPEC was obtained in a study of the toxicity of soluble NPECs of different composition in mice. From the data given in Table 3.6, it can be seen that the acute toxicity of NPEC with the index n = 0, 33 and 0.2 is significantly lower than the heparin-PVPB antagonist itself.

Table 3.6.

Acute toxicity LD50 (in mg / kg)

| Polymer | Day | | |
|---|---|---|---|
| | 1st | 2nd | 3rd |
| PMAC | 700 | 700 | 700 |
| PVPB | 98 | 60 | 54 |
| NPEC φ = 0,33 | 415 | 353 | 252 |
| NPEC φ = 0.2 | 566 | 406 | 406 |

Thus, the creation of a depot antagonist of NPEC heparins opens the possibility of obtaining low-toxic drugs. A significant reduction in the toxicity of polycation when it is included in the polycomplex indicates that in the body NPEC is stable and does not dissociate into separate components. This in turn means that the charged particles present in the blood, in particular proteins, do not displace PVPB from the complex. The latter agrees well with the results of the in vitro study published in paper [230].

In connection with the properties of non-dissociating NPECs described above, it is of interest to study the anti-heparin activity of **polymethacrylic acid (PMAC)** and PVPB complexes. Figure 3.8 shows the curves of turbidimetric titration of PVPB (1) and NPEC of different composition (2 and 3) with heparin [225]. As can be seen from Fig. 3.8, the reaction of polycation binding by heparin occurs irrespective of whether the polycation is free or bound to PMAC. When the heparin is added to PVPB and soluble NPEC heparin, phase separation occurs, and an equimolar polyelectrolyte heparin complex with PVEPB is released into the precipitate, as evidenced by elemental analysis of the precipitate: N / S 0.61, N / C 0.106; N / S 0.61, N / C 0.096 was calculated. Analysis of the supernatant shows that there is an insignificant (less than 10%) amount of PVPB, i.e., the polycation is almost completely transferred from PMAC to heparin. This means that the specific anti-heparin activity of the free and carrier-bound PVPB in aqueous solutions at pH 7.5 and ionic strength of 0.15 NaCl is practically the same.

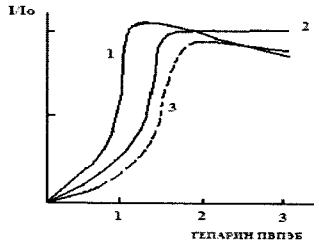



*Fig. 3.8. Curves of turbidimetric titration of PVPB and NPEC with heparin. 1-PVPB 2 * 10-4 M; 2-NPEC c = 0.33. Contains PVPB 2 * 10-4 M; 3-NPEC c = 0.2. Contains PVPB 2 * 10-4 M.*

Essential in titrating NPEC with heparin is that at any point, regardless of the amount of heparin added, the system contains NPEC (PMAC-PVPB) + IPC (heparin-PVPB) + free carrier (PMA-Na) and does not contain free



[illegible] i.e., depot, which is NPEC PMA-Na-PVPB, releases an anti-[illegible] drug exactly as much as heparin is added, keeping the rest of the [illegible] in a bound form, i.e., the depot, is sensitive to heparin [illegible] in the system. In other words, the depot releases anti-heparin [illegible] strictly equal to the therapeutic dose of this drug (see Fig. 3.6).

The above discussion on the principle of the effect of the depot of an [illegible]-heparin preparation is valid for the reaction between NPEC and [illegible] in an aqueous solution at pH 7.5 and ionic strength of 0.15 NaCl. [illegible] study of the mechanism of reaction in the body is difficult, however, [illegible] study of anti-heparin activity of PVPB and HTTEC in whole blood by [illegible]thromboelastography and in physiological solution allows one to indirectly [illegible]ge the course of the neutralization reaction of heparin in the body. Table [illegible] shows the values of neutralizing ratios expressed in Milligrams of [illegible]antagonist per 1mg of heparin (for NPEC neutralizing ratio is calculated in [illegible]relation to PVPB included in NPEC) obtained in experiments on [illegible]neutralization of heparin in physiological saline and whole blood.

Table 3.7.

Neutralizing ratios (in mg PVPB per 1 mg of heparin)

| Polymer | In a physiological solution | In blood |
|---|---|---|
| PVPB | 1 | 0,6 |
| NPEC | 1 | 1 |

These data indicate that, within the measurement error, the anti-heparin activity in the blood of the free-bound polycation is the same. In addition, the coincidence of neutralizing ratios in the blood and in physiological solution allows us to state that the neutralization reaction of heparin proceeds according to the scheme (see Fig. 3.6), both in aqueous solution and in whole blood, i.e., by the substitution reaction of PMAC with heparin NPECs do not have a significant effect on the protein and cellular elements of the blood; they are not competitors in the polycation binding reaction with heparin.

### 3.5. An interpolymer complex with eudragit marks E100 and L100, and proteases "C" with polyhexamethyleneguanidine

For several decades, copolymers based on methacrylic acid and methyl (ethyl) methacrylate, produced by the German company

RxhmPharma under the name Eudragi® (eudragit), used as auxiliary substances, have been widely used in pharmaceutical technology, mainly in the development of oral **dosage forms (DF)**. As the brands issued by the company, practically all the necessary options are considered, which include absorption of **medicinal substances (MS)** in the stomach (type E), in various parts of the intestine (types L and S), and in the technology of prolonged DF (types RL, RS and NE) [231]. Nevertheless, recently studies have been carried out to expand the use of produced polymers of the eudragit brand [232]. Given that most of the copolymers mentioned above are **polyelectrolytes (PE)**, one of the possible ways of modifying their structure is to incorporate them into the **interpolyelectrolyte complex (IPEC)** with the help of purposeful and scientifically grounded selection of oppositely charged polymers [12,57].

According to the specification of RxhmPharma, eudragit E (a copolymer of dimethylaminoethyl methacrylate and neutral methacrylic acid esters), soluble at pH <6, due to the hydration of protonated dimethylamino groups, is used in film gastrointestinal coatings. Eudragit L (a copolymer of methacrylic acid and methyl methacrylate) soluble at pH> 6, due to the ionization of carboxyl groups, is recommended for use as a film former in enteric-soluble shells [231]. At first glance, the interaction between them seems impossible, which, apparently, explains the absence in the literature of data on the formation of IPEC with the participation of two types of eudragits. Recently, only a few information has become available on the possibility of forming polycomplexes based on eudragites with other oppositely charged PE [232-234], not always with a detailed study of the formation conditions and composition of IPEC, but confining themselves to a statement of the formation of the polymer complex [235].

The types of eudragites studied in paper [232], being copolymers, dissolve at pH 6.0. Under these conditions, both PEs are ionized only to a small extent. Nevertheless, despite the low charge density and considering the ability of charging one component on another, the formation of IPEC seems quite possible.

Turbidimetric, viscometric and potentiometric titration was ascertained that the polycomplex is formed due to the separation of protons and the equimolar ratio of the reacting macromolecules. The scheme of IPEC formation is shown in Fig.3.9 [232].

Confirmation that the investigated PE interact in a ratio of 1:1 is the elemental analysis data presented in Table 3.8.

The obtained IPEC L100 / E100, according to infrared spectra, is an individual chemical compound-polycomplex stabilized by the cooperative system of salt bonds arising between ionized carboxyl groups L100 and



[illegible]ylamino groups E100 [232]. The revealed presence of non-ionized [illegible]ylamino groups, taking into account the preparation of IPEC in [illegible] of low charge density of the polycation, is quite natural and is [illegible] of their presence in the so-called "defective" - disunited sections [illegible]structure of the formed polycomplex, which is in complete agreement [illegible] literature data on similar chemical structure and the properties of PE [illegible]

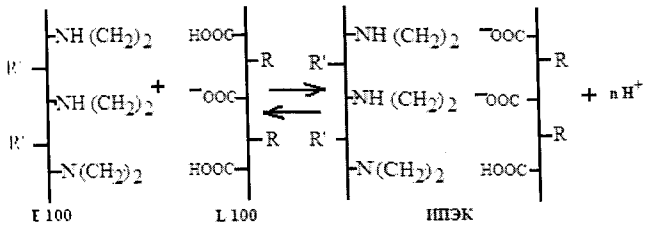



*Fig. 3.9. IPEC scheme between copolymers E 100 and L 100 at pH [illegible], where R and R ' are non-ionizable monomer units of copolymers.*

Table 3.8

**The composition of IPEC E 100 / L100 according to elemental analysis**

| № | Elemental analysis,% | | | Theoretically calculated element fraction,% | | | IPEC composition in moles z = [L100] / [E100] |
|---|---|---|---|---|---|---|---|
| | C | N | H | C | N | H | |
| 1 | 58,80 | 3,12 | 8,74 | | | | |
| 2 | 59,54 | 3,05 | 8,58 | 60,78 | 3,017 | 8,62 | 1/1 |
| Average value | 59,17 | 3,085 | 8,66 | | | | |

The study of the synthesized IPEC as a new polymer carrier will allow to expand the range of polymers produced by RxhmPharma company used in the development of oral dosage forms with controlled release.

In recent years, the direction to create dressings with combined biological effects has been intensively developing [236]. To treat purulent

wounds, pathogenetically justified is the use of wound coverings, which possess proteolytic and antimicrobial activity, which allows to significantly shorten the treatment time, reduce the consumption of medicines and eliminate the deficiencies that occur with native enzymes [237-239]. Among enzymes, complex enzyme preparations are more effective, including protease "C" [240].

A number of works [238,239,241,242] showed the possibility of obtaining transfer products of various forms (in the form of gauze and films) containing protease "C", an antibiotic or antiseptic and auxiliary substances that allow prolonging their biological effect. When the enzyme and the biologically active substance of another type are co-introduced into the carrier polymer, it is important to preserve the functional properties of the drug substances, in particular, the activity and stability of the enzyme preparation. In studies [241,242] on the joint immobilization of proteolytic enzyme "C" protease and high molecular weight antimicrobial substance **polyhexamethylenguanidine (PHMG)** [243], it was shown that the immobilized enzyme is activated and the CH-profile of the enzymatic action is changed. Therefore, it was of interest to investigate in more detail the effect of the composition of the polymer composition containing the protease "C" and the polymeric antimicrobial creature on the properties of the enzyme.

As polyelectrolytes, the salts of PHMG in aqueous solution participate in the interpolymer reaction with the protease "C" macromolecules with the formation of the polyelectrolyte complex (PEC), as a result of which the activity and stability of the enzyme immobilized in this way changes [242,244]. PHMG salts - PHMG hydrochloride (PHMG-X) with a molecular mass of 5.10 and 15 kDa and PHMG phosphate (PHMG-Ф) with a molecular mass of 10 kDa (RF, Pokrovsky Plant of Biopreparations), which are antiseptics with a long effect [243,245], and have excellent electrolytic dissociation constants (pK PHMG-X-5, PHMG-F-3), therefore, different behavior of these compounds in the complexation reaction with the protein, as well as differences in the properties of reaction products, should be expected [246].

In paper [246], the dependence of the activity and stability of protease "C" on the composition of the polymer composition was studied. According to the data obtained (Table 3.9), when an enzyme preparation and an antimicrobial substance are added to the composition in an amount of 0.1%, no significant stabilization of the enzyme can be achieved, while increasing their concentrations by a factor of 10, as a rule, OA considerably increase, the amount of stable form of the protease "C" immobilized as a result of complexation and residual activity.



As can be seen from Tables 3.9 and 3.10, the characteristics of the immobilized enzyme essentially depend on the composition of the compound, in particular on the type of antimicrobial substance and its molecular weight.

The kinetics of inactivation of protease "C" in compositions containing 1% of PHMG-X and 0.05-1% of the enzyme is described by semilogarithmic anamorphosis [247]. The greatest decrease in OA was observed as a result of complexation with PHMG-X with a molecular weight (MM) of 5 kDa (Table 3.10). However, the complexes formed with PHMG-X contain the enzyme in a stable form. At the same time, with an increase in the amount of the enzyme in the composition, the inactivation constant (Kin) initially decreased slightly, and then increased [246].

As a result of complexation with PHMG-X MM 15 kDa, the enzyme retains a high level of activity - 90-108%. OA and the content of stable form increase with the ratio of protease "C": PHMG. At the same time, the $C_{in}$ of stable form first increases, and then it tends to decrease, the $C_{in}$ of labile form is significantly reduced.

The kinetics of inactivation of protease "C" in a composition containing PSGMG-F is described by a curve with a maximum, which can be evidence of a restructuring of PEC accompanied by conformational changes and an increase in activity. It should be noted that in this case the composition of the composition has a slight effect on OA and the residual activity of the enzyme (Table 3.10).

When studying the dependence of the activity of enzyme-containing compositions on pH, a change in the enzyme activity profile was ascertained. It is known [248] that the displacement of pH-dependences is observed as a result of immobilization of enzymes independent of the charge of macromolecules of polymeric carriers, and a shift to the same region can occur both during immobilization on a polyanion and on a polycation. Thus, the change in pH-profile is explained not only by the effect of the electrostatic field of the polyion, but also by diffusion causes, conformational rearrangements.

Comparison of the results with the activity data given in Table 3.10 suggests that complex macromolecules of the polycation (pH of the solution of 8.5) participate in complex formation, which do not undergo significant conformational changes in the investigated pH range. Moreover, in the interpolymer reaction with PHMG-F all the components of the protease "C" can participate, with the exception of alkaline proteinase.

In general, the change in the pH profile of the protease "C" in complex with the PHMG salt, expressed in a higher level of enzyme activity in the

pH range corresponding to the wound medium, is a positive influence of the immobilization of the enzyme.

### 3.6. Structure and exchange properties of polycomplex bases for drugs prepared with carboxymethyl cellulose with urea-formaldehyde oligomers

In recent years, hydrophilic bases have been increasingly used in medicine. The expansion of the field of application of hydrophilic bases as an ointment base instead of edible fats and other deficient auxiliaries is explained by their ability to dissolve in water or almost unlimitedly to mix with it. This makes it possible to introduce significant amounts of aqueous solutions of medicinal substances into the hydrophilic bases, ensuring their high desorption from ointments [249]. In addition, much attention is paid to obtaining and developing ointment bases using large-capacity, cheap and affordable local raw materials.

The purpose of this section is to investigate the structure and exchange properties of a polycomplex (PC) - the basis for ointments and creams prepared with **carboxymethylcellulose (CMC)** with **urea formaldehyde oligomers (UFOs)**.

The purified sodium carboxymethyl cellulose salt of the Namangan chemical plant with substitution rates of 0.7 and polymerization 450 was used. The second component of the polycomplex refers to nitrogen-containing polymers. UFOs with linear and cyclo-chain structures were used in the work. The reaction mixtures were prepared from aqueous solutions according to the procedure described in paper [122]. The polycomplex base for ointments obtained with the help of CMCs and UFOs has pH = 6.0) 7.0.

The structure of the obtained products was ascertained (Fig. 3.10) using IR spectroscopy methods and based on literature data [158]. Analysis of the IR spectra of CMCs and UFOs shows that the components of the poly-complex bases for drugs are polyfunctional, the presence of $NH_4^+$, $NH_4^+$ (UFO), $COO^-$, COOH (CMC) groups in their macromolecules gives these polymers the characteristic properties of polyelectrolytes. **Intermolecular electrolyte complexes (IPEC)**, stabilized by ionic bonds between Na-CMC carboxylatanions and amino groups of the triazinone fragment of UFOs (Fig. 3.10, cr 3), are formed by mixing aqueous solutions of Na-CMC and UFO at pH 6.5.

IPEC are a new type of polymer compounds. Investigation of the structure and physicochemical properties of IPEC is important for



Table 3.9

**Effect of the composition on the relative activity and stability of the protease "C"**

| Substance* | The content of protease "C" / antimicrobial substance,% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0,1/0,1 | | | | 1/1 | | | | | |
| | OA,% | Residual activity After 5 hours,% | Amount of stable form,% | $C_{in}$ of stable form, h-1 | labile form, h-1 | OA, % | Residual activity after 5h,% | Amount of stable form,% | to" stable h -1 | $C_{in}$ is labile in shape, h-1 |
| PHMG-X MM 5 kDa | 56 | 31 | 71 | $1,76\text{-}10^{-2}$ | 1.25 | 72 | 52 | 100 | $1,7\text{ -}10^{-2}$ | - |
| PHMG-X mm 10 kDa | 56 | 40 | 100 | $1,8*10^{-2}$ | | 96 | 48 | 66 | $3,1*10^{-2}$ | 0,66 |
| PHMG-X MM 15 kDa | 66 | 14 | 32 | $3,3*10^{-2}$ | 1.15 | 100 | 72 | 77,6 | $1,2\text{-}10^{-2}$ | 0,39 |
| PHMG-F Not determined | 54 | 14 | 54 | $6\text{-}10^{-2}$ | 1,08 | 54 | 43 | | | |

* Content in composition of anti-microbial substance 1,0 %

Table 3.10.

**Effect of composition content on the activity of immobilized protease "C"**

| Content of proteases "C", % | OA,% of native | | | Residual activity after 24 hours,% of native | | | |
|---|---|---|---|---|---|---|---|
| | PHMG-X, MM, kDa | | PHMG-F | PHMG-X, MM, kDa | | | PHMG-F |
| | 5 | 10 | 15 | 5 | 10 | 15 | |
| 0,05 | 62 | 98 | 85 | 53 | 58 | 47 | 55 |
| 0.4 | 81 | 90 | 95 | 54 | 53 | 54 | 42 | 50 |
| 0.7 | 70 | 90 | 108 | 54 | 50 | 54 | 70 | 48 |
| 1.0 | 72 | 96 | 100 | 54 | 52 | 48 | 72 | 43 |

understanding the mechanism of reactions between oppositely charged polyelectrolytes and creating specific structural models of products of such reactions.

One of the main properties of a polycomplex base, obtained with the help of CMC and UFO, is the formation of a thin membrane when applied to the skin. As you know, grease-like medicines when applied to the skin and burn areas protect against the ingress of germs. However, it is known from the literature data that fat-like bases (petrolatum, lanolin, vegetable oil and others) have a number of drawbacks:

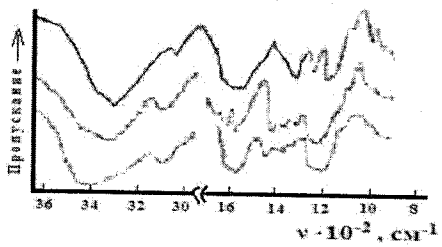



*Fig.3.10. IR spectra of UFOs (1), Na-CMC (2), and polycomplex the basis of the Na-CMC-UFO (3).*

Firstly, gas exchange, heat exchange, air exchange of moisture exchange of the skin are disturbed;

Secondly, Vaseline is not absorbed and is not washed off from the skin and linen.

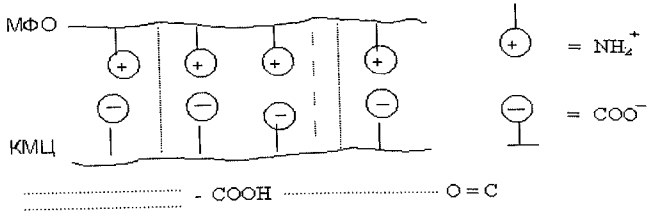
Therefore, it is of interest to ascertain how the base, obtained with the help of CMCs and UFOs, affects the exchange properties when applied to the skin. It should be noted that the basis obtained by us on the skin after 7-10 minutes forms a thin membrane. The influence of the membrane on the exchange properties of the skin can be determined by studying the dimensions in it. For this, the water-swelling and water permeability of membranes of polycomplex bases obtained with the help of CMCs and UFOs was determined experimentally. The water-repellency of membranes of polycomplexes was determined by the weight method. To study the swelling, rectangular membranes having an area of 9 $cm^2$ and a thickness of 70-80 μm were used. Samples were placed in closed bucks and filled with water and at regular intervals the sample was taken out of solution, blotted with filter paper, placed in a pre-weighed bag and weighed. The equilibrium degree of swelling was calculated after the increase in the mass



of the sample ceased. The mean values of the degree of swelling were determined from the results of three or five experiments. The error in the definition did not exceed 3-5%.

It is known [34] that the water swelling properties of a PC depend on the nature, the type of bonds and the geometric structure of the interacting components. In connection with this, we studied one of the main properties of PCs - the ability to swell in aqueous media, which is significantly dependent on the pH of the medium and the ratio of components. These studies are of great interest for the PC CMC-UFO of different structures in connection with the possibility of regulating their geometric structure and the nature of the bonds without changing the chemical nature of the original components.

Dependence of the degree of swelling of PC in aqueous media on the ratio of components is presented in Table 3.11. At an equimolar ratio of the interacting components of CMC with **UFO$_1$** (linearly branched structure) and **UFOt** (with triazinone rings), samples have the lowest degree of swelling, and in excess of one of the components (CMC or UFO), the swelling increases. Changes in the degree of swelling of CMC-UFO polycomplexes can be explained as follows. With an equimolar ratio of components, the interaction between macromolecules is greatest, i.e. between the components of the polycomplex there is a complete binding of CMC's to UFOs, stabilized by both hydrogen and ionic bonds, which lead to the formation of the maximum density of the grid (3.6). In this case, the smallest degree of membrane swelling of CMCs and UFOs is observed (Table 3.11). The presence of free functional groups of one or the other component with its excess leads to an increase in membrane swelling.




In the case of excess CMC content in the PC membrane, an increase in the degree of swelling is associated with the presence of free carboxyl groups (model a) [122]. It is interesting that UFOs do not swell by themselves; hydrophobic, but their presence in an excessive amount in the composition of the PC leads to an increase in swelling. Apparently, this is due to the excessive content of hydrophilic functional groups of UFOs and

to the increase in osmotic pressure in the capillary-porous structure of the PC (model b) (Scheme 3.7).

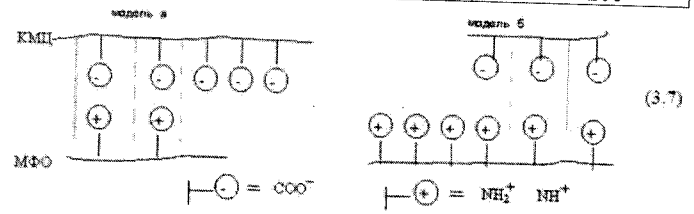
Table 3.11 shows that the more triazinone cycles in the UFO chain, the greater the swelling of PC membranes for all ratios of CMCs and UFOs. This indicates that the swelling capacity of these samples is largely determined by ionic bonds.

As it is known, polyelectrolyte complexes stabilized by ionic bonds have a greater degree of swelling [122] compared to polycomplexes stabilized by hydrogen bonds based on polycarboxylic acids [250,251]. Similar effects of changes in the degree of swelling were observed for the CMC-UFOl and CMC-UFOt multicomplex complexes, where the swelling is increased by a factor of 2-4 with an increase in the number of intercellular ionic bonds.

Table 3.11

**Swelling of polycomplex membranes depending on the ratio of components of CMCs and UFOs**

| UFO:CMC | Swelling of membranes in aqueous media, Q% | |
|---|---|---|
| | CMC-UFO | CMC - UFO t |
| 0,2 | 100 | 210 |
| 0,4 | 80 | 170 |
| 0.6 | 70 | 160 |
| 0,8 | 30 | 120 |
| 1,0 | 50 | 155 |
| 1,2 | 72 | 190 |
| 1,4 | 90 | 200 |




(3.7)

As noted, with the increase in cyclic fragments in the UFO chain, the PC structures are disordered, which was confirmed by the X-ray method [252].

As it is known [122,231], the water permeability (K) of polycomplex membranes depends on the hydrophilicity, the packing density of macromolecules and on the number of intermolecular bonds. The minimum



of "K" for the equimolar composition of CMCs and UFOs is related formation of the largest number of intermolecular hydrogen and ionic between the reacting components, which lead to an increase in the of crosslinks in the PC. An increase in the permeability of membranes with an excess of one or the other component is to loosening and formation of a heterogeneous porous structure. The hydrophilic functional groups CMC ($-COO^-$) and UFO ($-NH^+$, $NH^+_2$,) make significant contribution to the water permeability coefficient. The value of the coefficient of water permeability K for PC membranes of CMC-UFOs with a linear-branched structure is higher in comparison with PC membranes with 15% triazinone cycles in the UFO chain. Moreover, in all versions of the PC, the equimolar composition has a minimum value of the permeability coefficient, which is associated with an increase in the cross-link density. Using ultrafiltration data, the membrane pore size values were calculated by the Ferry equation [253]. Data on the calculation of pore sizes of membranes of polycomplexes and their composites are presented in Table 3.12.

Table 3.12.

**The pore sizes of polycomplex membranes depending on the ratio of CMCs to UFOs**

| UFO:CMC | The pore sizes in the membranes D *,A0 | The pore sizes in the membranes D *, A0 |
|---|---|---|
| | CMC-UFO 1 | CMC-UFO t |
| 0,2 | 400 | 130 |
| 0,4 | 350 | 80 |
| 0.6 | 330 | 76 |
| 0,8 | 300 | 70 |
| 1,0 | 330 | 75 |
| 1,2 | 338 | 92 |
| 1,4 | 345 | 110 |

** - pore diameter of polycomplex membranes*

The results of the experimental data show that the membrane pore sizes (D = 350-400 A) differ by 90-100 times in comparison with the sizes of water molecules (D = 3 Å and air molecules (O2, CO2, D = 5Å).

The observed experimental changes in the structure of polycomplex membranes as the UFO content increases in them can be most clearly traced to the methods of electron microscopy (Fig. 3.11). The fibrillar

structure of CMC (Fig. 3.11a) with the introduction of UFOs (Fig. 3.11b) undergoes changes accompanied by the formation of extended coil-shaped porous structures corresponding to the product of interaction from several tens of macromolecules (Fig. 3.11c). Clump-like - porous structure of PC can be explained by strong hydrophobization of the product of interaction of CMC with UFOs and because of screening of hydrophilic groups. These coil-shaped spherical particles have a rather narrow size distribution and their diameter ranges from 200 Å to 500 Å (Fig. 3.11c). Further increase in the UFO content in the PC leads to the formation of a heterogeneous structure, which is indicative of the formation of two phases of polycomplex and UFOs (Fig. 3.11g).

Investigation of the rheological properties of concentrated solutions of polycomplex gels was carried out on a rotational visco-meter "Reotest-2" in a system of coaxial cylinders in the stress range 2-380 Pa and shear rates from 1.5 to 13 * $10cm^{-1}$ at different temperatures. According to the results of rheological studies, the "viscous volume" V* or the average statistical size of the kinetic units was determined. The value of V * is a qualitative characteristic, which makes it possible to estimate the mobility of structural elements and their dimensions. V * was calculated by the formula:

$$V^* = \{2\kappa[E_\kappa/R-(\lg\eta-\lg A_\tau)T]\}/\eta\tau \qquad (3.8)$$

where k is the Boltzmann constant, R is the universal gas constant, t is the shear stresses, T is the absolute temperature, $A_\tau$ is the pre-exponential factor, $E_\kappa$ is the apparent activation energy determined from the slope of the lgn = f (T) dependence. The value of AT is neglected because of the very small value.

In paper [254], rheological properties were studied, the functional dependences log = f (logT), where η is the dynamic viscosity of the system, and τ is the shear stress. The graphically indicated function is expressed by the flow curve at various temperatures (298-343 °K) and shear stresses up to 380 Pa. The curves of the flow of aqueous solutions of Na-CMC and its polycomplex gels with urea-formaldehyde oligomers in the ratio of components (4:1) and (1:1) were also studied.

To study the structural-mechanical properties of Na-CMC solutions using a rotational viscometer (first with increasing, then with decreasing rotation), the rheograms shown in Figs. 3.12 and 3.13 were obtained. As can be seen from the figures, Na-CMC solutions exhibit thixotropic properties, a pronounced anomaly of the non-Newtonian viscous flow.



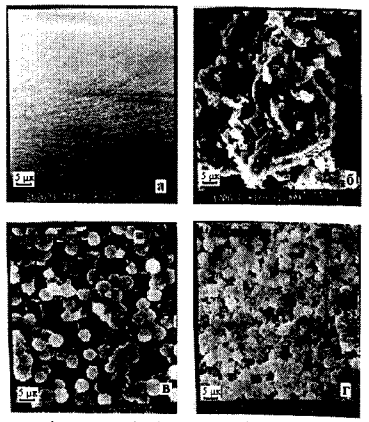


*Fig.3.11. Electron microscopic images of the surface of Na-CMC (a), UFO (b) and polycomplex bases with the molar ratio Na-CMC:UFO = 2:1 (c), 1:2 (d).*

From the standpoint of modern concepts of solutions of cellulose derivatives in various solvents, these substances form true solutions in which macromolecules are kinetically free. However, in the case of heterogeneity of cellulose esters in the degree of esterification of Na-CMC, their individual fractions will be poorly soluble. This is because the cellulose from which Na-CMC is prepared contains both amorphous and crystalline regions. During the preparation of alkylcellulose and its subsequent esterification, the distribution of the substituents along the cellulose chains can not always be uniform, since the internal highly crystalline regions react more slowly than the rest [255]. Therefore, in solution there is some quantity of non-molecularly dispersed Na-CMC, i.e., aggregates of macromolecules associated with each other in the same way as in the oriented crystalline regions of the original cellulose. As it is known [255], such crystallites act as gel centers, capturing a relatively large amount of molecularly dissolved Na-CMC and forming a three-dimensional lattice with the help of electrostatic or van der Waals forces. It is known from the literature data [256] that thixotronium of Na-CMC solutions is caused by the influence of gel centers. When the system undergoes a shear, some of the gel centers and their aggregates with individual macromolecules undergo destruction.

The effective viscosity decreases with time if the shear rate is constant. The structural destruction of thixotron solutions takes place under

these conditions at a measurable time. When the shear stress is removed, the structure of the thixotropic material again appears. When the solutions are at rest, the role centers can be re-aggregated (which happens in practice), while the apparent viscosity of the system increases. As it is known [255], depending on the structure of the existing system, the time for such reversion can vary from a few seconds to several days. It should be noted, that on rheograms (Figures 3.12 and 3.13) a clear "hysteresis effect" appears, which also indicates a thixotropy. Concentrated solutions of the investigated Na-CMC, like solutions of many other high-polymer compounds, are non-Newtonian liquids, i.e. in such solutions, the shear rate is not directly proportional to the shear stress.

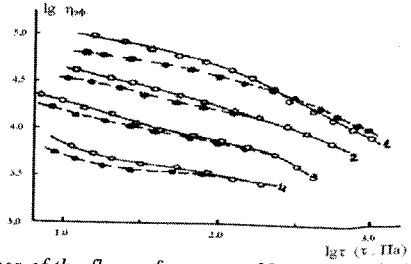



*Fig.3.12. Curves of the flow of aqueous Na-CMC solutions at different temperatures: 1 - 298 °K, 2 - 313 °K, 3 - 328 °K, 4 - 343 °K (dashed lines-hysteresis deviations of viscosity).*

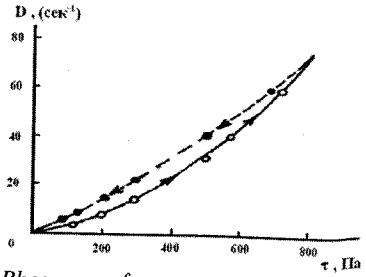



*Fig. 3.13. Rheogram of a concentrated Na-CMC solution.*

The process of complexation of Na-CMC macromolecules with urea-formaldehyde oligomers leads to significant changes in the structure of the polymeric matrix of polysaccharides, which leads, respectively, to a change in the rheological properties of the system of aqueous solutions (Figures 3.14 and 3.15). For equicomponent PCG solutions, the viscous parameters



and critical shear stresses are significantly reduced. Moreover, for systems of PCG Na-CMC with UFOs with a 1:1 component ratio, these parameters decrease more than for systems with a 4:1 ratio. These systems behave more like ordinary pseudoplastics. The investigated polymer complexes are obtained by mixing the ready-to-interact in the general solvent (water). Such a thixotropic effect under these conditions is a function of time, therefore, in order to obtain comparable results, all the experimental conditions were standardized, as the so-called displacement complexes. In this case, since the second component of the system is an oligomer (a much less low-molecular component of the complex), when mixing the Na-CMC rigid chain highly oriented polymer with the oligomer, highly oriented polymer complexes are formed in which the high-molecular matrix "controls" the organization of polymer associative systems and their complementarity. An important feature of "matrix-oligomer" systems is the ability to self-organization [15,122], which is expressed in the non-statistical distribution of oligomer chains between matrices, aspiration of short chains is more densely packed along the long macromolecule of the matrix.

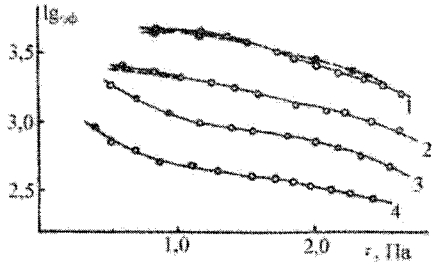



*Fig. 3.14. Flow curves of concentrated systems of PCG Na-CMC with UFOs (1:1) at different temperatures: 1 - 298 °K, 2 - 313 °K, 3 - 328 °K, 4 - 343 °K (dashed lines-hysteresis deviations of viscosity) .*

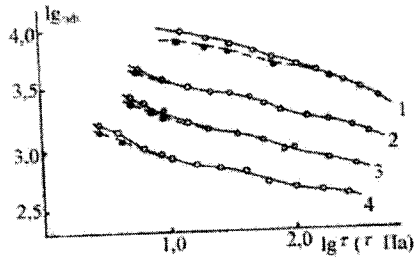



*Fig.3.15. Flow curves of concentrated systems of PCG Na-CMC with UFOs (4:1) at various temperatures: 1- 298 °K, 2 - 313 °K, 3 - 328 °K, 4 - 343 °K (dashed lines ~ hysteresis deviations of viscosity).*

This leads to the fact that, in the limiting case, part of the matrices will be completely occupied. This effect seems to determine the difference in the rheological behavior of the **PCG** systems with the ratio of components (1:1) and (4:1). As the results show, **polycomplex gels** exhibit new properties, different from the properties of the constituent components (Figures 3.14 and 3.15).

So for PCG, investigated in the work, thixotropic properties practically degenerate with a simultaneous marked decrease in viscosity characteristics. Studies have shown that solutions of Na-CMC are more structured, have higher viscosity characteristics, critical shear stresses, activation energy of viscous flow ΔEk = 55.7 kJ / mol. The temperature dependence of the viscosity for the PCG systems in the temperature range (298-343°K) for the component ratios studied is also described by the Arrhenius-Frenkel equation: $\eta = A * e^{\Delta Ek / R}$, where ΔEk is the apparent activation energy of the viscous flow (Fig. 3.16). The value of the apparent activation energy of the viscous flow for PCG, which is a measure of the intensity of the intermolecular interaction of macromolecules in solutions, in other words, the indirect character of the strength of the structure in solutions, is for PCG Na-CMC with urea-formaldehyde oligomers with a component ratio (1:1) ΔEk = 43.13 kJ/mole, and for the complex (4:1) ΔEk = 45.96 kJ/mole. Complexation of Na-CMC containing functional groups - carboxylataniones, hydroxyls and others with urea-formaldehyde oligomers leads to the development of polymeric associative systems in which the intensity of intermolecular interaction is much lower than in solutions of Na-CMC, due to which the strengths of structures are markedly reduced, and also decrease viscosity characteristics. The structure of the



polycomplex, which is directly related to the chemical nature of the polymer components, determines the degeneration of thixotropic properties in PCG, due to the surface screening of macromolecules and molecular associates of Na-CMC by oligomeric organized packings and sequences on polymer matrices.

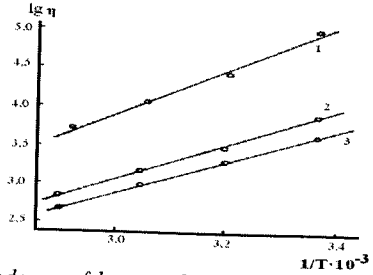



*Fig.3.16. Dependence of lg η on 1 / T concentrated solutions of Na-CMC (1) and polycomplex gels Na-CMC-UFO with the ratio of components 4:1 (2) and 1:1 (3).*

The interaction of chemically and structurally complementary macromolecules is of a cooperative nature. In this case, a linear (one-dimensional) sequence of single-type interchain bonds is formed, characteristic for cooperative systems of the simplest type. Apparently, it is possible to form a common cooperative system of two or more types of bonds, for example, ionic and hydrogen bonds. Because of the cooperative nature of the connections between heterogeneous polymer chains in the complex, the processes of their formation and destruction take place in certain intervals of external conditions. This is due to the fact that for the destruction (formation) of the interpolymer complex, a simultaneous rupture (emergence) of a large number of bonds is necessary, each of which may be weak (with low energy) for polymer-polymer (oligomer) interaction, types of equilibrium both at the macromolecular level and within the particles of the complex, which determines the time dependence of the formation of the polycomplex and the slow rearrangement of the intramolecular and supramolecular structures [15]. Large shear stresses lead to fundamental changes in the initial structure of the PCG. Each stress corresponds to a certain initial structure of the material and the elementary act of flow consists in the hopping of the chain segments from the new initial state to the activated one. As can be seen from the flow curves (Fig. 3.12-3.15), high stresses lead to significant changes in viscosity properties, and, accordingly, the structure of polycomplex systems. Based on the

results of rheological studies, the structural parameters of the magnitude of the "viscous volumes" V* or the mean statistical sizes of the kinetic units were estimated [256]. The values of V*, which are a qualitative characteristic that allows estimating the mobility of structural elements and their sizes, for water systems of PCG Na-CMC with urea-formaldehyde oligomers and for solutions of Na-CMC are given in Table 3.13.

The values of V*, which are a measure of the size and mobility of structural elements, as well as the transverse dimensions of the structural elements (B) for solutions of Na-CMC have slightly lower values than for solutions of complex systems. Such an increase in the size of the associates indicates the validity of the complexation of the anionic cellulose derivative with polycationic urea-formaldehyde oligomers. As the results show (Table 3.13), as the temperature increases, V* increases for N-CMC and PCG solutions, which is explained by the unfolding of macromolecules and the simplification of intermolecular interactions, as a result of which the dimensions of PCG associates increase. With increasing shear stresses to high values, gradual destruction of structural associates of supramolecular order and, accordingly, associates of PCG occurs. At small shear stresses (up to 10 Pa), the sizes of the structural associates of PCG exceed the sizes of the structural associates of Na-CMC, while at high shear stresses (up to 158.8 Pa), the values of the destroyed Na-CMC associates are slightly larger than the destroyed associates of PCG. From which we can assume that under the action of high shear stresses not only macromolecular associates of PCG are destroyed, but also the polycomplexes themselves.

Table 3.13

**The change in V * from temperature and shear stress (τ) for solutions of Na-CMC and PCG**

| τ, Pa | T,°K | Na-CMC | | PCG (1: 1) | | PCG (4: 1) | |
|---|---|---|---|---|---|---|---|
| | | $V*10^{23}m^3$ | $D*10^9$ | $V*10^{23}m^3$ | $D*10^9$ | $V*10^{23}m^3$ | $D*10^9$ |
| 10 | 298 | 927.2 | 210 | 1271 | 233.4 | 1340.6 | 237.5 |
| | 313 | 971.1 | 213 | 1328 | 237.0 | 1418.9 | 242 |
| | 328 | 1013.0 | 216.4 | 1399 | 240.9 | 1474.3 | 245 |
| | 343 | 1066.6 | 220.1 | 1464 | 245.0 | 1548.1 | 249 |
| 158.5 | 298 | 98.3 | 99.4 | 84.1 | 94.4 | 89.1 | 96.3 |
| | 313 | 102.4 | 100.8 | 87.4 | 95.6 | 93.4 | 97.8 |
| | 328 | 106.2 | 102.0 | 90.9 | 96.9 | 96.6 | 99.2 |
| | 343 | 110.5 | 103.4 | 95.2 | 98.4 | 98.5 | 99.5 |



Thus, the complex formation of the natural Na-CMC polysaccharide derivative with synthetic oligomers allows us to regulate the sizes of polymer associates and their properties. This opens up new ways of rational use of Na-CMC, and the process of complexation can be considered as a method of modifying a traditional polymer and regulating its molecular dimensions. The study of molecular complexes of a natural polymer makes it possible to establish the role of intermolecular interactions in the appearance of special properties and structure of complexes and the associated physico-chemical phenomena.

### 3.7. Study of the shelf life of polycomplex gels of carboxymethylcellulose with urea-formaldehyde oligomers as a basis for drugs

One of the tasks of modern pharmacy is the search for auxiliary substances with prescribed physico-chemical and pharmaceutical properties [200,234]. The following requirements are taken into account when selecting the bases for grease-like medicines: firstly, the substrate must be neutral, stable, compatible with medicines, do not have irritating, dehydrating and degreasing action, it is easy to remove by water, and secondly, it must provide emollient effect on the skin, so that the resorption of medicinal substances through the skin passes with the required speed for each individual case. Thirdly, when choosing the basis, one should take into account the cheapness, accessibility, ease of preparation of the dosage form, etc. [257,258].

In paper [259] have been mainly investigated the **polycomplex (PC)** and **polycomplex gels (PCG)** obtained with **sodium carboxymethyl cellulose (Na-CMC)** with **urea-formaldehyde oligomers (UFOs)**, which are used in pharmacy as the basis for ointments and soft medicinal forms [259]. It should be noted that the constituent components of the polycomplex are large-capacity, affordable, low-cost polymers [122].

Unlike traditionally used bases for ointments and soft dosage forms (from Vaseline), the base obtained with Na-CMC and UFO has great advantages: neutral pH, drug substances are well and evenly distributed in colloidal solutions of polycomplex gels (sulfur, furacillin, boric acid, gentamicin, etc.), it is easy and painless to simply flush with water from the skin, etc. [260]. It should be noted that the main difference between polycomplex Na-CMC and UFO gels as a basis for drugs is associated with their cheapness and availability, as well as large volumes of local industrial production.

One of the basic properties of the bases obtained with Na-CMC and UFO is storage stability. The stability of polycomplexes and polycomplex

gels obtained with Na-CMC and UFO by the method of capillary viscometry has been studied. To determine the stability of polycomplex bases at temperatures reflecting regional temperature fluctuations, viscometric properties of polycomplexes were studied in the temperature range 293 -323 K. Prepared samples for viscometric studies of three different compositions of Na-CMC (initial), Na-CMC-UFO, Na-CMC - UFO - glycerin after a daily standing for structuring were packed in glass jars with a capacity of 200-250 g with tightly screwed plastic caps. Samples for conducting viscometric studies were stored under thermostated conditions at different temperatures (T = 293°K -323 °K), and then cooled to room temperature. Viscosimetric changes at room temperature (293-295 K) were monitored by measuring the flow time of solutions of standard volume (V = const) through the capillary depending on the storage time under certain thermostated conditions. Experimental data showed that with increasing storage temperature, the stability period, that is, the onset of a change in Na-CMC viscosity and for Na-CMC-UFO polycomplexes, Na-CMC-UFO-glycerin decreases, which is associated with a change in the packing density of the macromolecule polycomplexes under the influence of temperature [261]. Indeed, the stability period of Na-CMC increases with increasing temperature from 293°K to 323°K (Fig. 3.17). When the Na-CMC solution is stored at T = 293°K, the onset of changes in viscosimetric properties is observed after 0.5 years, and at the same time at T = 323°K it is 10 days (Fig. 3.17). Analogous changes are also observed for polycomplex bases of Na-CMC-UFO (Fig. 3.18) and Na-CMC-UFO-glycerin (Fig. 3.19), but with a different character of the changes. Figure 3.18 shows that for polycomplex Na-CMC-UFO solutions at T = 293°K, viscosity stability is observed up to 2.5 years, and then shows a gradual decrease in viscosity, which indicates structural changes in the polycomplex.

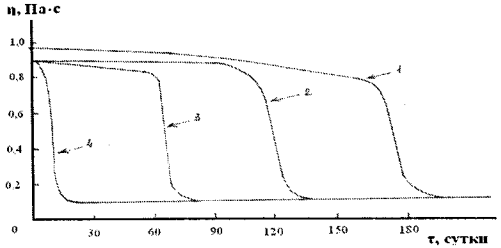



*Fig. 3.17. Kinetics of viscosity of solutions of Na-CMC heat-treated at different temperatures: 1 -293 °K, 2-303 °K, 3-313 °K, 4-323 °K.*



With increasing storage temperature, a decrease in the stability period can be observed, which indicates the onset of viscometric changes at a temperature of T = 323°K, which corresponds to 1.2 months. Such a character of the changes in viscosimetric properties is also observed for the polycomplex in the composition of Na-CMC-UFO glycerin. It should be noted that in the polycomplexes of Na-CMC-UFO and Na-CMC-UFO-glycerin, with increasing storage temperature, there is an acceleration of interaction between the constituent components of the polycomplex, which gives a peak at certain points of traffic (Fig. 3.18.3.19 cr.3.4).

From the viscometric data of polycomplex bases and constituent components, it is possible to deduce the expiration date of the bases used for ointments and soft medicinal forms, which are shown in the histogram in Fig. 3.20.

It can be seen from the histogram that with increasing storage temperature, the expiration date of polycomplex bases for three compounds decreases. At a temperature of T = 293°K, the stability of Na-CMC is 0.5 years, and in polycomplex gels Na-CMC-UFO and Na-CMC-UFO-glycerin, the stability period increases almost by 4-6 times.

Thus, the shelf life of the proposed polycomplex bases CMC-UFO and CMC-UFO-glycerin at T-293 °K is 2.5 and 2.8 years, respectively, which is in accordance with the regulatory and technical documentation.

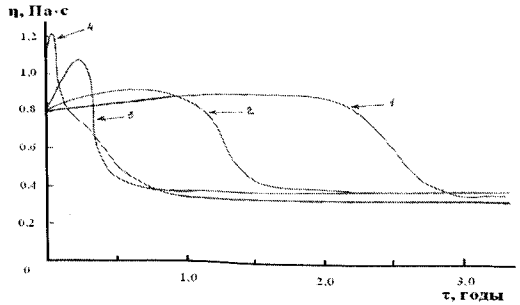



*Fig.3.18. Kinetics of viscosity of Na-CMC-UFO solutions heat-treated at different temperatures: 1-293 °K; 2-303 °K; 3-313 °K; 4-323 °K.*

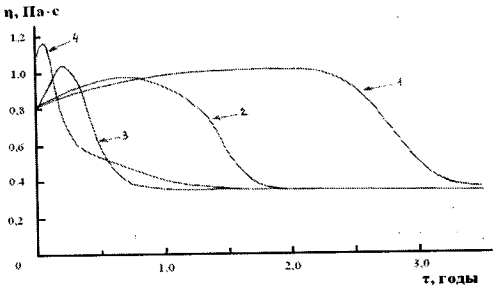



*Fig.3.19. Kinetics of the viscosity of solutions of Na-CMC-UFO-glycerin heat-treated at different temperatures: 1 -293 °K; 2-303 °K; 3-313 ° K; 4-323 °K.*

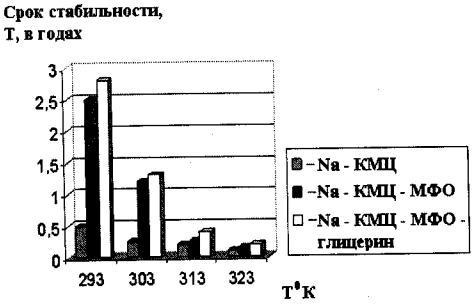



*Fig. 3.20. Histogram of the stability period of polycomplex gels obtained with Na-CMC and UFO.*



# CHAPTER 4. INTERPOLYMER COMPLEXES IN WATER AND AGRICULTURE

## 4.1. A short historical essay

The first attempts to create an artificial structure of soils with the achievement of modern science, in particular chemistry and technology, began in the late 40's and early 50's of the last century. To synthesize drug-structure-forming agents, high-molecular compounds-polymers, mainly derivatives of acrylic, methacrylic and maleic acids, were used.

Various US firms have developed VAMA (calcium salt copolymer vinyl acetate and maleic acid), Separan (hydrolyzed polyacrylamide), HPAN (sodium salt hydrolyzed polyacrylonitrile), etc. under the general name of crilium.

The results of long-term laboratory and field experiments have shown that on all soils the criliums increased the water resistance of the structure and the porosity of the aggregates, water permeability, plasticity, reduced water loss by evaporation, stickiness, cortex formation and erodibility, improved the germination of plant seeds, but did not always provide yield increases [262,263] . In England, GAFS-17 was synthesized, in the GDR - Ferdikung; in Italy - flotal, FRG-Rohagit, in Hungary-solrocrol, etc. [264].

Recently, polymeric structurizers and mulch materials have been widely used in agriculture. The use of water-soluble polymers (K, PAA, and LS polymers) as soil formers leads to an increase in water resistance from 5-10% to 50-70% [265,266], a decrease in the addition density [267], and an improvement in the hydrothermal regime [268] of the soil. There are contradictory data showing that excessive doses of polymers (eg, K-4) negatively affect on plants growth in the initial phases of development and in the harvest, despite the relatively high soil structure. In addition, the known structurants are carcinogenic in nature and do not degrade in the soil. The systematic introduction of these polymers can lead to their accumulation and, in this connection, undesirable consequences. Water-borne structure-forming agents are easily washed out of the soil, which, first, reduces the period of their working capacity, and secondly, polymer components with chemicals can harm nature.

Another method is known for improving the agrophysical conditions for growing plants and regulating the moisture reserves of the root layer of the soil-introducing various kinds of mulch material (peat, sand, coke dust, straw, polyethylene film, etc.). However, these types of mulch reduce the evaporation of moisture, close the soil from sunlight and contact with warm air, thereby reducing the temperature of the soil, which is undesirable for

plants in the spring period, since it usually does not have enough heat in the spring. Mulching cotton crops with a polyethylene film preserves the moisture of the soil, but does not interfere with its heating, which positively affects the development of plants and their yield.

The commonly used mulch materials, such as sawdust, straw, overgrown dry manure - sypsum, waste of various types of paper [269], photodegradable films [270] are scarce material, require huge labor costs and difficulties in mechanically introducing them into the soil.

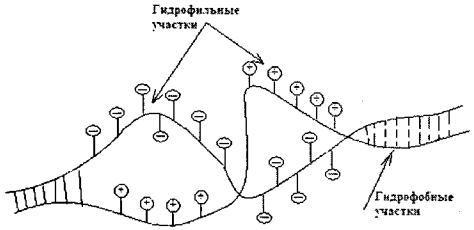
At the present time, a huge experimental material has been accumulated showing the effectiveness of polymer preparations in improving the water resistance of the structure of serozem soil types of the Republic of Uzbekistan [271].

With the development of new types of polymeric materials - interpolymer complexes new directions of scientific developments and their practical application in the agro-industrial complex of the national economy are outlined.

The first experiments on improvement of the structure of irrigated soils with the help of interpolymer complexes (IPC) were carried out in 1982. The effectiveness of IPC preparations exceeds the best world standards.

Interpolymer complexes and their composites are new, the latter generation of polymer materials. As a result of interpolymer reactions, new intermacromolecular compounds are formed that have properties different from those of the original components of the reaction.

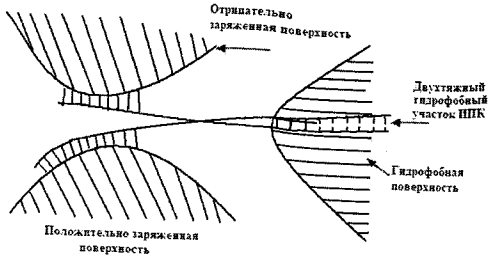
Interpolymer complexes contain hydrophobic regions composed of paired sections of complementary chains, and hydrophilic sequences of ionogenic groups formed by disjointed regions of oppositely charged polyions. The fragment of the IPC particle is depicted in the following scheme:



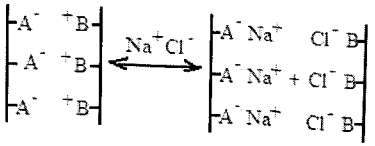

The presence of various (hydrophilic and hydrophobic) sites in the structure of polycomplexes gives them a unique opportunity. It is particularly evident in the case of contact with disperse systems. Because



different particles are differently fixed in microphases of those or other sites, give the material excellent properties. This can be schematized roughly like this:




IPC is introduced into the dispersed system by spraying the solution onto the surface of the soil (or soil) with the help of any watering technique. When the treated layer is subsequently washed with water, for example, when watering or when rain falls, the screening electrolyte is diluted and removed from the reaction sphere:




( 4.1)

In this case, the equilibrium of the reaction (4.1) shifts to the left; toward the formation of IPC. The resulting IPC gel can be repeatedly dried and moistened without deteriorating the adhesion properties, i.e. quality bonded layer. Various low molecular weight organic and inorganic substances, for example, fertilizers, plant growth stimulants, herbicides and other physiologically active compounds can also be included in the IPC gels. To do this, simply add them to the stock solution. Immobilized in IPC substances can then be released from polycomplexes into the environment at a controlled rate.

Due to these properties: polycomplexes have been successfully used as soil formers to prevent their water and wind erosion while simultaneously increasing fertility. In the soil-polymer crust, the particles of the dispersed phase will be bound together by a thin IPC interlayer. Such crusts do not collapse under the influence of strong wind and rain.

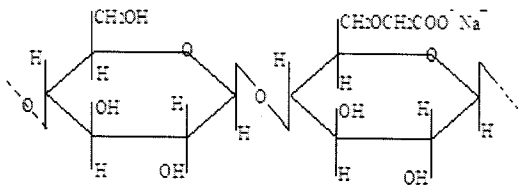
## 4.2. Characteristics of the main drugs

Polymeric materials used on irrigated sierozems and other soils should have the ability to dramatically increase the water resistance of the macrostructure, reduce the deficit of organic matter caused by erosion, and also the erosion of soils, and increase the yield of cotton.

By the time of our research, the theoretical aspects of soil interaction with interpolymer complexes - structure formers were not developed enough, so it became necessary to conduct numerous laboratory, vegetative and field experiments to test the most promising and available polymeric materials.

Taking into account the soil properties, the following polymeric materials were used for the preparation of interpolymer complexes:

**Carboxymethyl cellulose (CMC).** Samples of CMC of Namangan chemical plant, obtained by heterogeneous solid-phase charging of sulfite wood pulp with monochloroacetic acid (GOST 5,588-79) with substitution degrees (SD) 0.7 and polymerization (SP) 400, were taken as the main object of the study. The fragment of the structure of the CMC macromolecule can be as follows:



(4.2)

CMC is a weak polyacid, the dissociation constant of which depends on SD. When the SD varies from 0.1 to 0.8, the dissociation constant varies from 5.25 * 10-7 to 5 * 10-5 [272]. In practice, in general, CMC is used in the form of Na-salt (here and everywhere Na-CMC).

**Urea-formaldehyde resin (UFR).** For laboratory studies, UFR obtained in the presence of ammonia was used [133]. For practical purposes, industrial samples of urea-formaldehyde oligomers of the brand **CFVR (carbamide-formaldehyde viable resin)** and **CFLTR (carbamide-formaldehyde low-toxic resin)**, representing a 60-70% solution, were used for practical purposes. Condensation products of urea and formaldehyde CFVR and CFLTR have the following physicochemical data for certificate №1004 (Table 4.1):



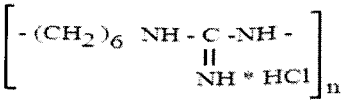
Table 4.1.

**Physico-chemical characteristics of CFVR and CFLTR**

| Characteristic | Indicators |
|---|---|
| Appearance | Homogeneous suspension from white to light yellow without foreign impurities |
| Gelatinization time:<br>a) at 373 K per second<br>b) at 293 K in hours | <br>45-70<br>10 |
| The concentration of hydrogen ions (pH) | 7-8,2 |
| The miscibility of the resin with water at (2001)°C in a 1:2 ratio by volume | Full |
| Refractive index | 1,463 |
| Specific weight, g/cm$^3$ | 1,28 |
| Viscosity according to VZ-4 | 25-60 |
| Free formaldehyde content,% | not more than 1 |

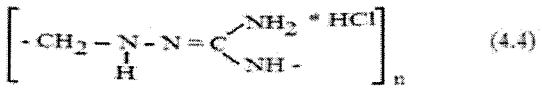
*The product corresponds to GOST 14231.*

**Polyhexamethyleneguanidine (PHMG).** In the work, samples of PHMG with a polymerization degree of 400 with the following structure were used [273]:



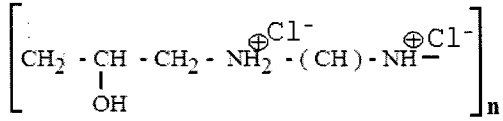
(4.3)

**Polymethyleneaminoguanidine (PMAG).** PMAG was prepared according to the procedure [274] with a polymerization degree of 20 with the following structure:



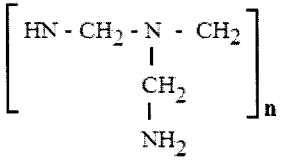
(4.4)

**Oligomer obtained on the basis of dichlorohydrin with hexamethylene diamine (DCH-HM).** DCH-HM was obtained at the Tashkent Institute of Chemistry and Technology by polymerizing dichlorohydrin with hexamethylenediamine [275]:



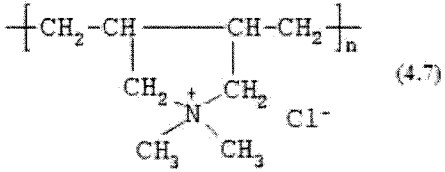
(4.5)

**Polyethylenimine (PEI).** Branched PEI of the brand "Polymin R" (FRG) with a weight average molecular weight of 60,000 was used in the work.



(4.6)

**Poly-N, N-demyldiallylammonium chloride (PMDAACH).** DMDAACH was obtained at the Institute of Inorganic Chemistry of the Russian Academy of Sciences [276]. A sample with [s] = 0.8 dl/g was used in the work.



(4.7)

**K-4.** K-4 was obtained by hydrolysis of polyacrylonitrile with alkali sodium at a component ratio of 2.5:1.0. The polymer is produced by the Chirchik industrial enterprise of "Elektrokhimprom". K-4 is a viscous solution of cream color with 10% content of polyacrylonitrile.

**Methods for determining the agrophysical properties of soils treated with IPC**

To determine the effectiveness of the influence of IPC on the agrophysical properties of soils, optimal compositions, doses, timing and ways of introducing IPC into the soil were determined; their influence on



soil structure, growth, development and yield of cotton was studied; laboratory, vegetative, micro- and microdelay, production experiments were carried out.

**The water resistance of the soil structure** was determined by the Pavlov method [277]. The essence of the method is to determine the number of waterproof aggregates remaining after a ten-minute soil soak in the water, as well as 20-fold mixing by turning the vessel, relative to the original quantity of soil treated and untreated by various interpolymer complexes, taken as a sample for analysis.

In order to have an idea of which of the units turned out to be waterproof, water with a soil sample is passed through a set of sieves having a size of 5 mm and up to dimensions of 0.1 mm. This makes it possible to determine the fraction of aggregates, for example, in the interval 0.1-0.25 mm, remaining after soaking against the entire initial mass of soil (sample). This percentage can also be expressed in percentages.

**The mechanical composition** was determined by treatment with sodium hexamethophosphate by the method of Bratcheva [277].

The soils contain minerals montmorillonite, illite, baidellite, mica, quartz, etc. in the form of crystals and their fragments. The same or different crystals of minerals are combined into particles, which are called mechanical elements.

Determination of the mechanical composition of soils is necessary for the analysis of physical and mechanical properties, since to each type of soil there corresponds an inherent mechanical composition. Analysis of the mechanical composition of soils consists in decomposition of aggregates of 20 g of soil to the size of mechanical elements by boiling it in water for an hour in the presence of sodium hexametaphosphate. The soil sample thus acquires a state of dispersion, the calculation of the percentage content of particles of different sizes in certain intervals, and is an analysis of mechanical composition.

Microaggregate analysis of the soil was carried out according to the Kachinsky method [277]. The microaggregate analysis of the soil according to Kachinsky differs from the aggregate analysis by the Pavlov method in that the soil sample becomes soaked for a longer time, namely 24 hours, as a result of which a higher dispersion of the particles is achieved and, in addition, smaller screens are taken, namely 0.1 mm and 0.05 mm, while the number of smaller dimensions is determined by the rate of their fall in the water.

**To establish the effect of the chemical composition** of IPC on cotton seedlings, laboratory-miniature experiments were carried out in 0.5-liter beakers in a 6-fold replication. The IPC was tested in aqueous solutions of

various concentrations. The experiments were carried out with both distilled and ordinary water. Observations led to the growth of the stem root, the lateral rootlets, the main stem and the appearance of these leaves.

**The effect of the treatment of the soil surface of the IPC on the erodible soil** was studied using the Gussac method [278] on the 8D hydrodrive. The method is based on the erosion of 100 $cm^3$ of soil (screened through a 1 mm sieve) with a water flow rate of 4.5 $cm^3/s$ per 1 cm of width sample.

**Vegetative experiments.** The experiments were laid using the technique of UzRCI [279] in vessels with a height of 30 cm in diameter and a surface area of 706.5 $cm^2$. The soil in the vessels was filled with a density of addition of 1.3 $g/cm^3$. The dose of polycomplex is 0.02% of the mass of the soil. Experiments were laid down according to the scheme: 1) Soil + NPC - BACKGROUND; 2) BACKGROUND + IPC surface application; 3) BACKGROUND + IPC in the 0-5 cm layer; 4) background + IPC in the 0-15 cm layer; 5) BACKGROUND + IPC in the 0-30 cm layer.

Field small-scale, large-scale production experiments were carried out according to the technique of UzRCI [279] in various cotton-growing farms from 1997 to 2005. Phenological observations were conducted in accordance with the methodology [279].

### 4.3. The influence of interpolymer complexes on the erosion and anti-deflation resistance of soils

The anti-erosion and anti-deflation effects of interpolymer complexes (IPC), of course, depend both on the properties of the soils themselves and the characteristics of the IPC. In addition, a certain role is played by the methods of addition, dose and concentration of the IPC solution.

The mechanical composition, organic matter of the soil, pH of the medium (the content of hydrogen ions) has a significant effect on the structure-forming effect of IPC.

The anti-erosion effect of IPC increases with increasing dose, but the effectiveness of the IPC unit is reduced. The interval of doses of IPC, in which the high efficiency of the IPC unit still remains, is identified as optimal. The interval of optimal doses of one or another IPC on different soils is different.

The increase in the lumpiness and water resistance of soil aggregates, as well as the adhesion between them, simultaneously leads to an increase in the roughness of the soil surface, its water permeability, anti-erosion and anti-deflation resistance.



Therefore, in order to quantify the complex effect of all factors on the efficiency of IPC, it is necessary to identify and quantify the change in the properties of soils that cause the erosion effect.

The anti-erosion resistance of the soil, which is understood as the resistance of the soil to the washing action of the water flow, is determined by the weight in the water separated by the streams of particles and by their adherence to each other.

In agriculture, the erosion resistance of the soil, as a rule, is estimated by the value of the bottom eroding flow velocity. For its calculation, the authors of the paper [280] proposed a formula whose main arguments are the size of waterproof aggregates (d) and interaggregate coupling (c).

This relationship can be used to assess the effect of interpolymer complexes on the soil erosion resistance of soils, when applied simultaneously, the water resistance of the structure and interaggregate adhesion change. Such conditions are usually observed in the treatment of IPC sputtered and compacted soils without their subsequent loosening. In other cases, the erosion resistance of soils depends only on the size and water resistance of the structural units.

For loose soil (bulk density less than 1.25 $t/m^3$) a more simple form:

$$V_{\Delta p} = 1{,}55 \sqrt{\frac{q}{n\gamma_0}\,\gamma - \gamma_0\; d\;\left(1 - \frac{P}{100}\right)}, \qquad (4.8)$$

Where: n - is the roughness coefficient;
q-water discharge in the irrigation sulcus, $m^3/s$;
$\gamma$, $\gamma_0$ - coefficients of runoff of treated and untreated soils;
d-size of water-resistant aggregates, m;
P - dose of the drug.

Dependence (4.8) finds practical application not only for the assessment and mapping of erosion resistance of soils, but also for the forecast of its increase in the processing of soil by artificial structures and subsequent loosening of soils [281].

According to the dependence (4.8), the magnitude of the bottom erosion velocity is proportional to the square root of the aggregate diameter ($V_{\Delta p} \sim \sqrt{d}$). Therefore, for the arable horizons of soils not connected by plant roots, the following ratio can serve as a measure of the effect of IPC on the erosion resistance of soils:

$$\frac{V_{\Delta p_n}}{V_{\Delta p}} = \overline{\frac{d_n}{d}}, \qquad (4.9)$$

where - $V_{\Delta p}$ d and $V_{\Delta pn}$) $d_n$ - respectively, the bottom eroding velocity and weight-average diameter of water-resistant soil aggregates before and after IPC treatment with the drug.

Field tests of the anti-erosion effect performed by the introduction of interpolymer complexes based on carboxymethyl cellulose (CMC) and urea-formaldehyde resin (UFR) (aqueous solution) of different concentrations on the surface of loose soil, in order to create a protective layer 10-12 cm wide and 80 -100 m thick without further loosening showed the validity of the correlation (4.8).

In this case, the weight-average diameter of the water-resistant aggregates was determined in the samples after the drying of the protective layer formed on the surface of the soil treated with IPC. It is ascertained that the destruction of soil under the influence of raindrops begins when the stress from the impact of the drop reaches the ultimate strength of the soil [282]. Note that the ultimate strength of the soil depends on the mechanical strength and water resistance of soil aggregates, as well as on the adhesion between them. The quantitative characteristic of the ultimate strength of the soil can be the permissible (indestructible) velocity of rain drops.

For soils with interaggregate cohesion, the approximate value of the permissible (nondestructive) velocities of raindrops can be ascertained by the following simple relationship [282]:

$$V_{c.per} = \overline{\frac{0{,}7ms}{\rho}}, \qquad (4.10)$$

where $V_{c.per}$ - is the permissible (nondestructive) velocity of rain drops, m/s;

c - cohesion of soil in a state of complete water saturation, determined by the method [282], t/m$^2$;

m - is a coefficient that takes into account the reduction in friction due to friction;

p is the specific mass of water, t/m$^3$.

According to the equation (4.10), the effect of the IPC on the permissible droplet drop rate is estimated by the relation:



$$\frac{V_{c.per.s}}{V_{c.per}} = \overline{\frac{S_{per}}{S}}, \qquad (4.11)$$

where, Vc. extra-shortly.п., $S_{per}$-permissible speed of drop and grip of soil, treated IPC.

For unconsolidated loose arable horizons of soils, the size of the admissible (nondestructive) velocity of raindrops is determined, mainly, by the strength of the structure:

$$v_{c.per} = 1{,}5 \cdot 1010^3 d \qquad (4.12)$$

The effectiveness of the IPC action in this case is described by the relation:

$$\frac{v_{c.per.s}}{v_{c.per}} = \frac{d_s}{d} \qquad (4.13)$$

where $\vartheta_{c.per.s}$, $\vartheta_{c.per}$ - permissible (non-destructive) speed of rain drops in case of their falling onto the soil, treated and untreated IPC;

$d_s$ is the weighted average diameter of the water-resistant aggregates of the soil before and after IPC treatment.

Having ascertained the change in the permissible velocities, it is possible to approximately estimate the effect of the IPC on the permissible droplet size and rain intensity.

According to V.Shmit's simplified formula [283] for estimating the change in the allowed droplet size, we obtain the following expressions:

for cohesive soils:

$$\frac{v_{c.per.s}}{v_{c.per}} = \frac{S_{per}}{S} \qquad (4.14)$$

for soils without clutch:

$$\frac{v_{c.per.s}}{v_{c.per}} = \frac{d_s^2}{d^2} \qquad (4.15)$$

where $v_{c.per.s}$ - the permissible droplet size for the treated and untreated IPC soil.

To ascertain the average droplet size, depending on the rain intensity, one can use an equation of the form:

$$d_{av} = ki\, g^n \qquad (4.16)$$

where $d_{av}$ - average diameter of drops, mm;
$i$ - intensity of rain, mm/h;
$k$ - empirical coefficient, varies from 0.92 to 1.34;
n - the exponent varies from 0.18 to 0.21.

Then the influence of IPC on the permissible rain intensity at which there is no significant disturbance in the structure of the soil, it can be approximately determined from the following relationships: for soils with a cohesion:

$$(\frac{i_{r.per.s}}{i_{r.per}})^{0,2} = \frac{S_{per}}{S} \qquad (4.17)$$

and for non-cohesive soils:

$$(\frac{i_{r.per.s}}{i_{r.per}})^{0,2} = (\frac{d_s}{d})^2 \qquad (4.18)$$

where $i_{r.per.s}$ - permissible rain intensity before and after IPC soil treatment.

Further, the questions of the influence of IPC on the anti-deflation resistance of soils were studied. Note that usually iodine is the antideflation resistance of the soil, its ability to withstand wind blowing is understood. The criterion for assessing anti-deflation resistance is considered to be the rate of the onset of mass movement of soil particles ($V_m$). For loose soils that do not have interaggregate cohesion in the case of an equalized soil surface, the value of old age ($V_m$) is calculated on the basis of the results of determining the aggregate composition of the soil according to the formula [284]:

$$V_{mz} = 2{,}4\frac{lg\frac{z}{z_0}}{lg\frac{1}{z_0}}\ \overline{l\frac{d_v - p}{60\quad p}\cdot g}, \qquad (4.19)$$

where V is the rate of onset of mass movement of soil particles, related to the height z above the soil surface, sm/s;

$l_{60}$ -weighted average value of aggregate sizes from zero to magnitude, curve of aggregate composition, cm;

$d_v$ is the density of soil particles, g/cm$^3$;

p is the air density, g/cm$^3$;



g - acceleration of gravity (g = 981 sm/s$^2$);

$z_0$ - is the parameter; depending on the size, the protuberances of the roughness lugs cm ($z_0$ = 1/30).

If we assume that the change in the density of aggregates and soil during its processing with IPC is insignificant and can be neglected, we obtain the following expression:

$$\frac{V_{mzn}}{V_{mz}} = \frac{lg\frac{z}{z_{on}}.lg\frac{1}{z_0}}{lg\frac{z}{z_{on}}.lg\frac{1}{z_0}}\ \frac{\overline{l_{60n}}}{l_{60}} \qquad (4.20)$$

Where $V_{mzn}$- the rate of onset of mass movement of soil particles, related to the height z above the surface of the soil treated with IPC, provided that the size of the protrusions on its surface is related only to the size of the aggregates composing it; $l_{60}$- weighted average value of the size of aggregates having a value from zero to a size corresponding to 60% of the cumulative curve of aggregate composition; $z_{on}$ is the parameter of the surface roughness of the soil treated with IPC. Its value is $0.07L_{60n}$, $L._{60n}$ is the size corresponding to 60% of the cumulative curve of the aggregate composition of the soil after the introduction of IPC.

According to the aggregate analysis of the soil before and after its treatment with IPC, substituting the parameters in the relationships (4.20), after carrying out the corresponding calculations, we obtain data on the evaluation of the influence of the IPC of the structure-forming type on the deflation resistance of the soil. Based on the results of our studies, as well as the literature data, the following should be noted: the optimal dose of IPC should be considered as such, after application, which the intensity of soil loss due to erosion, deflation or joint manifestation does not exceed the rate of soil formation. Usually such a condition is observed in the case when the magnitude of the speed of the water or air flow does not exceed the increase in the so-called permissible (according to the condition, indissolubility or non-reflation) speed. For the same soil, the permissible speed: in the case of water streams:

$$v_{\Delta per.} = \frac{v_{\Delta\rho}}{1{,}23} \qquad (4.21)$$

in the case of air currents

$$v_{per.} = \frac{v_m}{1{,}23}, \qquad (4.22)$$

$\vartheta_{\Delta r}$, $\vartheta_m$ - respectively, the bottom erosion velocity of the water flow and the speed of the air flow at which the mass advance of soil particles begins.

These characteristics of anti-erosion and anti-deflation resistance, as well as the allowable rate of rain drops, are the main criteria on which to base when choosing and calculating the optimal doses of polymers.

After the experimental determination of water resistance, lumpiness, interaggregate cohesion before and after IPC soil treatment, it is possible to proceed to calculate the values of the rates of movement of water and air currents and the permissible velocities for soils treated with different doses of IPC.

The optimal dose of IPC can be set graphically. The calculated values of the water flow rates and allowed velocities for the soil are plotted on the graph and the velocity dependences are plotted against the dose of the IPC. In the field of positive action of IPC due to the increase in the size of waterproof aggregates and, consequently, the increase in the roughness and water permeability of the soil, the value of the bottom speed of the water flow will decrease with increasing dose of IPC. At the same time, the permissible speed for the IPC treated soil will increase (Figure 4.1).

The dose of the IPC corresponding to the intersection point of the curves is assumed to be optimal. Such a procedure is valid in the case of choosing the optimal doses of IPC to prevent soil deflation, as well as in the case of determining the permissible characteristics of raindrops. In addition, in order to save polymer preparations, the proposed method can be used to determine the optimal doses of IPC when differentially applied along the length of the slope.

It is known [284] that, with rain erosion, the flow velocity increases down the slope. Therefore, having constructed a series of graphs of the dependence of the bottom flow rate on the dose of IPC for different sites of the slope, it is possible to determine the appropriate number of optimal doses of IPC corresponding to them.

If data on the rate of soil formation are known, the optimal dose of IPC should be determined based on the allowable soil loss value. It is especially advisable to apply this for areas of joint manifestation of storm and irrigation erosion, as well as deflation.

The most important element of the anti-erosion technique of furrow irrigation is the allowed (by the condition of indissolubility) water flow into the irrigation groove. The condition for the inadvertibility of the furrows also corresponds to the permissible flow velocity ($\vartheta_{\Delta per.}$). For known values of weighted average diameter, specific gravity and porosity of soil



aggregates, before and after treatment of its IPC, the magnitude of the permissible velocity is calculated from formulas (4.8), (4.21).

The value of the average permissible velocity and depth of the stream are found in the following relationships: at 7 <H / d = <350 for beds of furrows with an unexpressed geometric roughness

$$v_{per.} = \frac{v_{\Delta per.}}{0{,}92\,\frac{d_n}{H}^{\frac{1}{6}}} \qquad (4.23)$$

$$H = \left(\frac{1{,}17 \cdot v^2 \Delta per. \cdot n_n^2}{d_n^{1/3} \cdot J}\right)^{\frac{1}{3 \overline{n_{n+0{,}67}}}}, \qquad (4.24)$$

at 3 <H = d <28, which is typical for furrows treated with IPC, these calculated dependences have a slightly different form:

$$v_{per.} = \frac{v_{\Delta per.}}{1{,}14\,\frac{d}{H}^{\frac{1}{4}}} \qquad (4.25)$$

$$H = \frac{v^2 \Delta per. \cdot n^2{}_n}{1{,}25 d_n^{1\,2} \cdot J}^{\frac{1}{3 \overline{n_{n+0{,}67}}}}, \qquad (4.26)$$

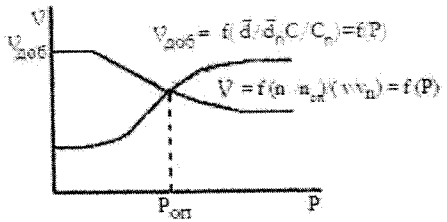



*Fig. 4.1. Dependence of flow rates ($\vartheta$,$\vartheta_{per}$) on the dose of polymer.*

where H is the depth of the stream, m;

$d_{,,}$ is the weighted average diameter of water-resistant soil aggregates after treatment with IPC, m;

$\vartheta_{per.}$ - average permissible flow velocity, m/s; - bottom permissible flow velocity, m/s;

$n_n$ is the Pavlovsky roughness coefficient;

J-slope of irrigation groove.

Having obtained for each value a slope corresponding to the depth of the stream, we calculate the area of the live section (ω, $m^2$).

Knowing the permissible average speed and area of the live section, we find the allowable water flow ($q_{per}$, $m^3/s$);

$$q_{per} = v_{per}\omega \qquad (4.28)$$

For small inclines, the results obtained should be checked by the condition of non-transfusion of furrows, using the technique [285].

The next step in the calculation is to determine the value of $\alpha_n$:

$$a_n = a(\frac{d}{d_n})^{0,174}, \qquad (4,29)$$

where α, $\overline{d}$ and $\alpha_n$, $\overline{d}_n$ are, respectively, the values of the exponents in the water absorption formula and the weighted average diameter of the water-resistant aggregates of the soil before and after its treatment with IPC.

Having ascertained the value of α and using empirical relationships:

$$l = k_1 \ \overline{q_0}\ , \qquad (4.30)$$

and

$$\kappa_1 = 1000a^{1,43} \qquad (4.31)$$

where 1- is the length of the furrow, m; $q_0$-water flow rate, l/s, $k_1$ value, different for soils of different mechanical composition (for sandy loam - 167, for light loamy soils -260, for medium-loamy soils - 370 and for heavy loam -600), we determine the optimum length of irrigation groove treated with IPC $l_n$:

$$l_n = 1000a_n^{1,43}\ \overline{q_{per.}}\ . \qquad 4.32$$

The length of the water run-up to the end of the furrow ($t_{ln}$) is determined from the dependence:

$$t_{ln} = \frac{8,55 \cdot a_n^{1,43}}{\overline{q_{per}}}, \qquad (4.33)$$

where $q_{per}$ is the water flow, l/s, which is lowered (by the condition of indissolubility of the soil). The duration of irrigation (t, h) can be determined by the formula:



$$t = \frac{aml_n}{3600q_{per.}}, \qquad (4.34)$$

where m is a given irrigation norm, expressed as a layer of water, m; a-the width of the rows, m. The remaining designations are the same.

You can also set the topping time (tg), i.e. the duration of irrigation after running up the irrigation water front to the end of the furrow:

$$tg = t - t_l, \qquad (4.35)$$

where $t_l$ - is the time for water to reach the end of the furrow, h.

Having ascertained approximate data on the main elements of the anti-erosion irrigation technology on furrows treated with different doses of IPC, you can later proceed to the calculation of optimal doses of the preparations.

By applying in the field conditions or on a model in the laboratory different volumes of the IPC solution of a given concentration, a solution volume per unit area ($Q_{„}$) is ascertained experimentally, which provides a prescribed depth of soaking.

In accordance with the change in the weighted average diameter of the aggregates relative to the initial value of the aggregate, the elements of the furrow irrigation technique are calculated from the formulas proposed above. Based on the results of the calculations, the optimal combination of irrigation technology elements is chosen with the smallest (permissible) concentration of IPC (Cg), which meets the requirements of practice.

To prevent erosion of the sidewalls of the sulcus, the width of the treated IPC of the bottom of the sulcus should exceed the perimeter of wettability (g). The value of this indicator should be calculated taking into account the hydraulic flow parameters in the head part of the irrigation groove, i.e. at its greatest filling.

Approximately, the value of the perimeter of wetness can be determined from the empirical relationship:

$$p = \frac{\omega}{R} \approx 3,0 \cdot R^{0,68}, \qquad (4.36)$$

where ω - is the live section of the flow in the head part of the furrow, $m^2$; R-hydraulic radius in the same range, m.

After this, it is possible to determine the optimal dose of IPC ($D_{opt}$) of a day of one irrigation sulcus:

$$D_{opt.} = Cg \cdot Qn \cdot \rho \cdot 1_n, \qquad (4.37)$$

where Cg is the allowable concentration of IPC, kg/m$^3$; Qn-norm of the IPC solution, providing a depth of soaking (2-3 mm) and expressed as a layer, m; p-perimeter of wetness, m; $l_s$-length of the section of the furrow, drawn by the IPC, m.

The optimal dose of IPC per hectare of irrigated field (Nn) is:

$$N_n = \frac{10000}{ml_n} D_{opt.} = \frac{10000 \cdot Cg \cdot Qn \cdot \rho}{m}, \qquad (4.38)$$

where $N_s$ is the optimal dose of IPC per hectare of irrigated field, kg/ha; m- row spacing, m. Other designations are the same.

It is known [285] that the amount of water flow along the length of the furrow decreases and in some location may not exceed the permissible flowrate for untreated IPC soil ($q_{per.fl}$). Then the length of the treated bottom of the irrigation groove is equal to:

$$x = 1 - \frac{q_{per.fl.}}{q_0} \cdot \frac{t}{t_{l_n}}^{a_n} \cdot l_n, \qquad (4.39)$$

where x - is the length of the treated bottom of the irrigation groove, corresponding to the equality $q = q_{per.fl}$, m; $q_0$ - water flow in the head part of the irrigation sulcus, m$^3$/s; t - watering time, h; $t_{ln}$ - is the length of the irrigation groove treated with the IPC.

The optimal dose of IPC decreases in ln/x times. However, such a reduction in the dose of IPC during furrow irrigation is possible under the condition of an insignificant change in the uniformity coefficient of moistening, i.e. a slight difference in the volume of absorbed water at the beginning and end of the furrow.

The approximate value of the humidification uniformity coefficient h- can be determined from the relationship:

$$\eta = (\frac{t - t_l}{t})^{1-a}. \qquad 4.40$$

The designations are the same.

In conclusion, it should be noted that the estimated calculation of the effectiveness of IPC preparations does not exclude the need for an experimental study of the effect of IPC on the basic erosion properties of the soil. As a result of the experiments, it can also be concluded that it is



quite possible to further develop computational methods and improve the accuracy of existing calculation schemes for assessing the anti-erosion and antideflation effects of IPC.

### 4.4. The use of interpolymer complexes and composites as antifiltration screens

The purpose of this section of the monograph was to create anti-filter screens using IPC to increase the efficiency of irrigation water use and improve the conditions for the development of a number of crops (cotton, etc.)

Note that the known ways to reduce water filtration with the creation of anti-filtration screens with additives of surfactants [286], organomineral substances, etc. [287,288] are economically inexpedient and, in addition, require the displacement of large masses of soil, substances to create an anti-filtration screen. Reclamation with the use of anti-filtration screens made of perforated polyethylene pipes located below the ground at a depth of about 50-55 cm is also not very profitable.

It should be pointed out that in the conditions of our republic none of the above methods has found wide practical application. In this regard, we have developed a simpler method that takes into account the use of well-swelling, ultrafiltration properties of new IPC.

High sorption and swelling properties, as well as low values of the permeability coefficient of films of interpolymer complexes, have made it possible to use them for creating anti-filtration screens. The ability to adjust the above characteristics by changing the nature of the components, their ratio, the charge density in the circuit, and the compatibility of the starting components and the pH of the medium opens the way for the production of polycomplex materials as required.

For the creation of anti-filtration screens, IPCs and their composites having high swellability and low permeability were selected. Low value of IPC film strength and composites in this case does not matter; when applying the solution, a soil-gel screen is formed (on the substrate - soil), which is used to reduce filtration.

In laboratory experiments on the effect of IPC screens on the filterability of the soil, we used a 24 cm sieve and a special lot installation. The sieves and trays were filled with light loamy soil, after which the soil was thrombosed slightly and then wetted with water (to obtain a natural volumetric weight).

A comparison of the filtration capacities of various soils was carried out by determining the rate of descent of the water level contained above

the surface of the studied soil. In hydraulic engineering and in irrigated agriculture, this speed is usually designated "k" in m/h or in mm/min. It is also possible to compare the filtration rate through the time t of the determined amount of water that protrudes above the soil surface at the initial moment of the experiment to a height h. Under laboratory conditions, the height h was 22.1 mm, and the amount of water, 1 liter.

The results of the investigation of the filtration rate "k", as well as the filtration time t in soils treated with IPC, are presented in Table 4.2.

Table 4.2

**Dependences of the speed and time of filtration on the treatment of light loamy soils with an interpolymer complex**

| Ordinal number infusion | amount water, liter | Ordinary soil (control) | | Polycomplex application to the soil surface | | Polycomplex application at a depth of 40 cm | |
|---|---|---|---|---|---|---|---|
| | | к , (mm/ min) | t, s | к , (mm/ min) | t, s | к , (mm/ min) | t, s |
| 1 | 1 | 110,5 | 12 | 51,00 | 26 | 94,70 | 14 |
| 2 | 1 | 88,4 | 15 | 31,57 | 42 | 69,70 | 19 |
| 3 | 1 | 60,3 | 22 | 21,73 | 61 | 29,40 | 45 |
| 4 | 1 | 55,2 | 24 | 13,95 | 95 | 21,90 | 63 |
| 5 | 1 | 33,1 | 40 | 8,89 | 149 | 12,70 | 104 |
| 6 | 1 | 30,1 | 44 | 4,60 | 288 | 5,50 | 244 |
| 7 | 1 | 26,0 | 51 | 4,30 | 302 | 3,69 | 359 |
| 8 | 1 | 24,9 | 53 | 3,28 | 404 | 2,70 | 485 |
| 9 | 1 | 23,6 | 56 | 2,85 | 465 | 2,37 | 559 |
| 10 | 1 | 22,4 | 59 | 2,63 | 504 | 2,00 | 665 |
| 11 | 1 | 22,4 | 59 | 2,28 | 580 | 1,87 | 707 |
| 12 | 1 | 22,4 | 60 | 2,88 | 580 | 1,87 | 710 |

From the results of the conducted experiments it follows that the filtration rate of irrigation water and its escape to sub-plow horizons is weakened by a factor of 10-12 in soils treated with a polycomplex. In experiments conducted in field conditions, it was found that this attenuation



occurs not less than 2.5 - 3 times at a dose of the polycomplex of 15-20 g/m³. This is quite enough to reduce the unproductive water losses in crop irrigation in the conditions of Central Asia by the same amount.

Thus, the results of the studies prove the high feasibility of the wide application of the polycomplex in cotton-glaze irrigation to create an intrasoil screen. As a result, it is possible to significantly reduce the irrigation rates, hence, to achieve a significant saving of irrigation water.

Taking into account the tests in the future, we also conducted experiments in the field, especially to study the influence of polycomplexes on the reduction of deep water filtration by creating intrasolar screens (Fig. 4.2).

We have developed an assembly that provides a screen at a depth of 35 ~ 40cm. The unit consists of a hinged plow device, which is hung on the tractor MTZ-80 and DT-54 (Figure 4.2). On the underside of each heap, tubes are welded, to which two sprayers are attached. The polycomplex solution is supplied to these tubes through hoses connected to a tank or tank mounted on a tractor [289,290].

With the beginning of the tractor's movement, the plow device descends and the tap for opening the polycomplex solution opens. After cutting the soil of the soil with a blade at the required depth on the surface of the soil under pressure generated by the UGS compressor, a solution of the polycomplex was sprayed from the sprayers, and the next dump was filled with soil. As a result, at the depth of the dump after drying (drying time about 20-25 days), a continuous filtering screen in the form of a film was formed in the soil (Fig. 4.2).

Note that the "operation" described above is carried out simultaneously with the plowing of the field itself. Cotton is planted according to the established rules of agricultural technology.

In 1999-2005 we set up the field experiments in Brigade № 9 of the Uchkhoz TIIM and in the Brigade № 7 named after Kim Pen Khwa of the Middle-Chirchik District of the Tashkent Region in light loamy soils. The area of the experimental site was 0.85 hectares, and the control plot was 1.2 hectares. Accounting for the water supplied to zero was made using the weirs of Chipoletti and Thomson.

Water permeability of the studied soil is high - steady filtration occurs 2-3 hours from the beginning of absorption and is 0.72 m/day.

As a result, we found that to maintain the presumed moisture in the layer with a depth of 0.7-0.7 m 0.7-0.7-0.6 of the lowest moisture capacity (HB), three irrigations were carried out according to the scheme 1 - 2 - 0 for Experimental plot and four watering schemes 1-2-1 on the control plot. The inter-irrational periods in the vegetation phases were 28-30 and 20-23

and 20-23 days, respectively. The modes of watering cotton, the parameters of elements of irrigation technique and watering efficiency are presented in Table 4.3.

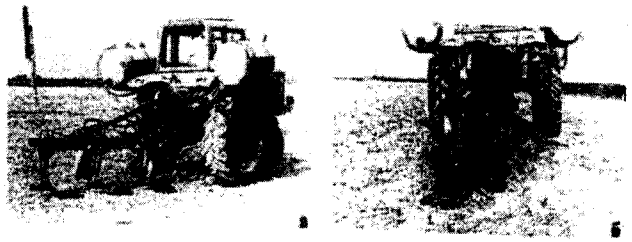


*Fig. 4.2. General view of the mechanism for creating an anti-filter screen (a) and the general form of the mechanism in work (b).*

Table 4.3.

**Modes and parameters of the irrigation technique and the efficiency of watering cotton on the experimental and control sites (furrow length 270 m)**

| room glaze | Consumption water, l / s (*) | Time, hour | | | Irrigated standards | | Coefficient of good deed, % | Losses, % | |
|---|---|---|---|---|---|---|---|---|---|
| | | Before run up | Before wetting | Total | Gross, mg 3 / ha | Net, $m^3$ / ha | Gross | on evaporation | for filtration |
| Experimental site | | | | | | | | | |
| 1 | 0,9 / 0,45 | 2,35 | 5,72 | 8,07 | 1040 | 880 | 84,6 | 0,30 | 15,1 |
| 2 | 0,85 / 0,45 | 2,44 | 5,55 | 7,99 | 1015 | 825 | 81,2 | 0,23 | 18,57 |
| 3 | 0,85 / 0,40 | 2,38 | 5,68 | 8,06 | 954 | 760 | 79,6 | 0,28 | 20,12 |
| Control plot | | | | | | | | | |
| 1 | 0,9 / 0,45 | 2,79 | 6,28 | 9,25 | 1222 | 850 | 69,6 | 0,33 | 30,17 |
| 2 | 0,85 / 0,45 | 3,12 | 6,25 | 9,37 | 1214 | 810 | 66,7 | 0,25 | 33,05 |
| 3 | 0,85 / 0,40 | 3,05 | 6,19 | 9,24 | 1126 | 780 | 69,3 | 0,27 | 30,43 |
| 4 | 0,80 / 0,40 | 3,16 | 6,08 | 9,24 | 1102 | 715 | 64,9 | 0,26 | 34,84 |

*Note: (*) - numerator - in the run-up period; denominator - during the wetting period;*

It can be seen from the table that when cotton fields are watered in fields with an anti-filter screen, the depth filtration decreases by 10-15% compared to the control one. A sharp increase in soil moisture was observed when watering with large norms in the control section.

During irrigation of cotton, there were no discharges of irrigation water. At irrigated gross rates in the experimental area of 900 -1040 $m^3$/ha and at the control plot - 1100-1250 $m^3$/ha, the humidification of the soil layer located below the calculated one was, respectively, from 150 to 205 m 3 / ha and from 350 to 420 $m^3$/ha.

The irrigation norm in the experimental area was 3009 $m^3$/ ha, and at the control plant -4664 $m^3$/ ha, the yield of raw cotton was 33.8 c /ha and 29.2 c /ha, respectively. Observance of the optimal irrigation regime in fields with an anti-filter screen made it possible to obtain from cotton sales by 38978 soums/ha more than in the control variant. Reducing the depth of filtration during watering of cotton allowed to save 553 $m^3$/ha of water for three irrigation and the value of the rate of the fourth irrigation.

Experiments on the study of soil irrigation regimes with an anti-filter screen on the surface were carried out in combination with soil and agrotechnical conditions. Irrigation was carried out along furrows, to the bottom of which a polycomplex was applied.

Field tests were conducted under the same conditions on a number of two experimental and control sites located at an area of 1.0 and 1.5 ha, respectively. Irrigation was carried out along furrows with a length of 160 m and a row spacing of 0.6 m, a slope of furrows 0.002 0.003.

We note that a 3% solution of the polycomplex was applied to the bottom of the furrow at a rate of 0.5-0.8 liters per 1 $m^2$ of surface. The water flow in the furrow in the control section was 0.7-1.2 l/s, in the experimental section 0.5-0.8 l/s.

In experiments on the uniformity of the field humidification, the

polycomplex was applied to the second half of the length of the furrows. The uniformity of the harvest was estimated from the volumes of irrigation norms distributed by the soil moisture content.

As a result of our experiments, it was found that applying IPA solutions at the end of the furrows leads to a reduction in irrigation gross rates with a reduced water flow rate. At the same time, the efficiency of irrigation technique increased from 0,55 to 0,7, and the saving of irrigation water was 250 m 7 ha with each watering (Table 4.4).

Table 4.4

**Duration and norms of irrigation, efficiency of irrigation technique cotton in the control and experimental areas**

| room glaze | Water flow, l / s (*) | Duration of irrigation, min. | | | Speed ext., m /min | Norms of irrigation, m $^3$/ha | | | | efficiency technicians glaze $m_{(nm)}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Before run up | Before wetting | Total | | Before run up | Before wetting | Total $m_{(6p)}$ | m | |
| Control plot | | | | | | | | | | |
| 1 | 1,2 / 0.8 | 84 | 147 | 231 | 1,66 | 605 | 710 | 1315 | 720 | 0,54 |
| 2 | 1,0 / 0,8 | 104 | 142 | 246 | 1,53 | 625 | 680 | 1305 | 720 | 0,55 |
| 3 | 1,0 / 0,7 | 98 | 154 | 252 | 1,63 | 590 | 650 | 1240 | 720 | 0,58 |
| Experimental site | | | | | | | | | | |
| 1 | 0,8 / 0,6 | 98 | 155 | 253 | 1,63 | 474 | 560 | 1034 | 720 | 0.69 |
| 2 | 0,8 / 0,5 | 101 | 180 | 281 | 1,58 | 486 | 540 | 1026 | 720 | 0,70 |
| 3 | 0,8 / 0,5 | 94 | 168 | 262 | 1,70 | 452 | 505 | 957 | 720 | 0,75 |

*Note: (*) - numerator - in the run-up period; denominator - during the wetting period;*



From the table it follows that watering the cotton along the furrows, on the bottom of which the polycomplex is applied, makes it possible to significantly reduce the gross rates by 250 m$^3$/ha for three irrigation and increase the efficiency of irrigation techniques from 0.55 to 0.7. At the same time, the yield increase was also increased by 4 c /ha compared to the control plot [291,292].

At the same time, it should be noted that in spite of significant water savings, the implementation of this method of irrigation is somewhat difficult in practice. This is due to the fact that after each irrigation, when the agrotechnical treatments are carried out, the films are destroyed, and therefore a repeated application of the polycomplex is necessary. Consequently, the carrying out of cotton irrigation on fields with a continuous intrasoil anti-filter screen, as shown above, is less labor-consuming and more effective.

When applied to the surface of the soil, IPC solutions not only bind soil particles to aggregates, but also substantially modify them, in particular, the hydrophilicity of the soil changes, and this contributes to the in-filtration of water and acts as depressant for evaporation.

Since pure water is an extremely important environmental factor of the environment, without which it is impossible to develop plants purposefully, it is necessary to take it very carefully. We should also note that the normal development of seedlings, shoots and the development of young cotton plants occurs when the moisture content of the root layer of the soil fluctuates in the range 70-100% of the marginal field moisture capacity. As an excess, hack and lack of soil moisturizing negatively affect the vital activity of the cells of the bioorganism.

On the basis of data on the study of moisture evaporation from soils, it can be concluded that treating the upper soil layers with an IPC solution leads to the formation of a soil-polycomplex mulch that protects the underlying soil layers from drying out. Figure 4.3 shows that the structured soil evaporates the water to a much lesser degree, and in the control for three days the moisture evaporates rapidly and on the fourth day the moisture content in the soil drops to 4% (Figure 4.3, cr. 1). In soils treated with IPC (Fig. 4.3, cr. 2), the formed soil-polycomplex layer (0-5 mm) lying on the microstructural layer dries quickly and the capillary connection of lumps with the underlying aggregates breaks off. This, in turn, leads to a decrease in the evaporation of water and an increase in the period of the moist state of the underlying layers of soil for 6-7 days.

Thus, it can be concluded that our interpolymer complexes and composites allow us to purposefully create anti-filtration screens to reduce irrigation water norms.

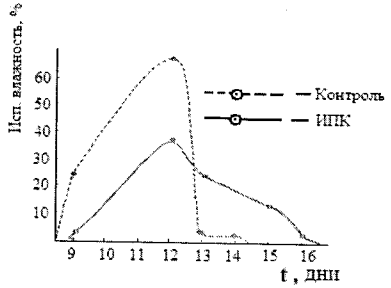



*Fig. 4.3. Evaporation of soil moisture (laboratory experience).*

### 4.5. Application of interpolymer composite materials for infiltration irrigation and hydrogels

As described above, IPCs stabilized by both hydrogen and ionic bonds are formed during the interaction of CMC solutions and various polycations (UFR, PMAG, PGMG, etc.) [122,289]. By changing the conditions for carrying out the complexation reaction, the relationship and nature of the interacting components, it is possible to obtain IPC and composites with the corresponding hydrophobic and hydrophilic regions in the microstructure.

The ability of swelling of IPC composites in aqueous media determines the possibilities of their practical application as hydrogels ("piggy banks" of water) in the soil. We studied samples of IPC composites of various compositions, which were swollen in equilibrium in salt-free aqueous media at pH = 6 [293,294].

In our further research, we set out to create hydrogels and corresponding composites with dispersed fillers due to non-stoichiometric IPCs for increasing the efficiency of irrigation water use and improving the conditions for the development of crops (cotton, etc.).

The high swellability corresponds to the region Z>0.5, therefore, IPC composites were used precisely in such proportions of the components.

We found that IPC composite hydrogels, changing the water-physical properties of soils, reduce the water yield by 4 times, increase the life-time of productive moisture by 80%. The water-retaining capacity of hydrogels contributes to a several fold increase in moisture reserves in the active soil layer. This, in turn, significantly increases the period of conservation of soil moisture [295].

We conducted field studies on the use of IPC composite hydrogels to



study the water saving in cotton fields on the fields of the TIIM training and experimental farm. Experimental sites were selected on three fields of 0.4 ha each with IPC composite hydrogels introduced in 1997-2000. For the study, we used the technique of UzRCI with triplicate repetition in two directions - to study the effect of IPC composite hydrogels on soil moisture and irrigation regime, as well as on phenology.

Hydrogels with a swellability of 800-1200% were introduced into the soil of each experimental site at a depth of 0.2-0.4 m, in a liquid or powdery state, in amounts of 50 kg/ha. The operative determination of soil moisture made it possible to determine the timing of irrigation, which were carried out according to the scheme 1-0-1 at 0.7-0.7-0.6 HB. It should be pointed out that the active layer was 0.6 and 0.7 m in the first and second waterings, respectively. In the studies of 1998 and 1999, when using hydrogels, it was possible to reduce the number of irrigation in the trial plot to two waterings when the control was three and four, respectively. The irrigation norm of the water for these years was 2650 $m^3$/ha and 2479 $m^3$/ha on the experimental plot, and at the control plot 5130 and 4150 m3 / ha.

To study the effect of groundwater on the supply of plants with moisture, observation wells were ascertained at the experimental and control sites. As a result of observations of the groundwater level (GWL), it was observed that groundwater, if it lies at a depth of 1.5-1.8 m in cotton supply, does not play a significant role and does not participate in the accumulation of moisture with hydrogels. The study of its direct effect on plants showed that the IPC hydrogel promotes intensive growth of both the above-ground and root parts of agricultural crops. In addition, apparently, it is very important that the gel does not suppress the microflora of the soil and is not destroyed by bacteria.

If there is a hydrogel in the soil with a water supply, in addition, it is also possible to substantially stop the "water stress" of the plants. In soil mixed with IPC hydrogel, even after 20-40 days after watering, moisture is maintained above critical. If there is a gel in the soil, the level of its normal humidity can be maintained by reducing the number of irrigation, therefore, to achieve a significant saving of irrigation water.

With the aim of solving an important ecological task, namely, saving water, as well as improving the technique and technology of irrigation, we have developed methods for obtaining interpolymer composite materials with dispersed fillers.

The quality of watering crops depends largely on the uniformity of wetting the irrigated area, i.e. from the uniformity of water distribution along the length of the irrigation groove, and with a smaller irrigation norm. In this regard, in 1997-2002 laboratory and field studies were

conducted in TIIM and its training and experimental farm, in the Syrdarya region using **interpolymer composite materials** (ICM) as infiltration irrigation. Irrigation was carried out on trays made of ICM composition with dispersed fillers, which look like a furrow and are installed on the furrow ridges next to the cotton. Trays were made using special molds (Figure 4.4).

Several trays with different pore sizes were made, which were placed one after the other along the furrow at a distance of the run-up length of the irrigation water. Water savings were achieved through exclusion of water discharge, as well as ensuring uniform moistening of the soil along the entire length of the furrow. The procedure for using the irrigation tray was as follows: water from the distributors (Figure 4.5) (1), through a filter (2) made of a polymer composition, enters the micropores of the tray and through it into the soil. The flow rate of water is regulated by the size of the micropores (3). Filter (2), prevents clogging of trays. Note that usually irrigation water enters the soil through the pores of the tray in the form of droplets. The width of the trays is 10 cm, the depth is 12 cm, and the length is 100 cm. By connecting them in series, you can dial any desired length.

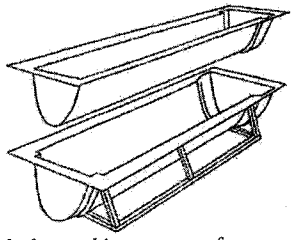


*Fig.4.4. Molds for making a tray of composite material.*

We determined the distribution of irrigation norms over the soil layers, according to the variants of small-scale experiments, in triplicate repetition, we will further indicate that irrigations were carried out without a discharge. The soil properties of the site were automorphic, and in terms of texture - medium loam. The rate of water absorption into the soil was 0.016-0.017 m / h. The level of moistened soil layers at the beginning and end of the furrow was 50 and 45 cm at the first, 62-51 cm in the second and 81-69 cm in the third watering, respectively.

The balance equation of irrigation norms is compiled [289,296]:

$$M_{fr} = m_1 + m_2 + m_3, \qquad (4.41)$$



Where: $M_{fr}$ - irrigation rate applied to the site, $m^3$/ha; $m_1$ - calculated irrigation norm, $m^3$/ha; $m_2$ - loss of water for evaporation, $m^3$ / ha; $m_3$ - soil humidification below the calculated layer, $m^3$/ ha.

The irrigation norms for the layers were determined by the soil moisture content before and after irrigation, after 3.5-7.10 and 15 days, and were calculated according to the formula:

$$m = 100\,Hd\ \ P_{lm} + P_f\ , \qquad (4.42)$$

where, H is the calculated layer of soil, m; d is the density of the soil, g/$m^3$; $P_{lm}$, $P_f$ - humidity at the least moisture capacity and actual before watering, % of the mass of dry soil.

When carrying out watering with water consumption of 0.4-0.6 l/s at irrigated gross rates of 600-650 $m^3$/ha, when the norm below the design layer was 20-35 $m^3$/ha (3.3-5%), and the loss water for evaporation - 30-33 $m^3$/ha (5%), the calculated irrigation norm will be equal to 550-581 $m^3$/ha. The application of small irrigation norms to 600 $m^3$/ha and compliance with irrigation regimes ensured a significant increase in yield (by 3.4 c/ha), in contrast to the control plot.

So, we can conclude that the results of both laboratory and field tests of the IPC and composite materials obtained by us fully confirm the validity of the scientific results and the effectiveness of our developed technologies for the production of these products - polymer complexes. Next - the task of wide implementation in practice of the scientific and technical and technological results achieved by us.

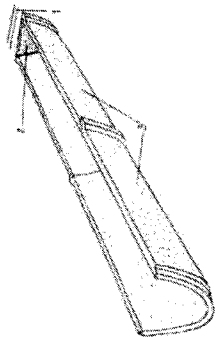


*Fig. 4.5. General view of the tray made of composite material.*

## 4.6. The use of interpolymer complexes based on carboxymethylcellulose and amine-containing polymers and oligomers for fixing soil

In the interaction of solutions of carboxymethyl cellulose (CMC) and amine-containing oligomers and polymers, IPCs stabilized by both hydrogen and ionic bonds are formed, the ratio of which can be regulated. By changing the conditions for carrying out the complex formation reaction and the nature of the interacting components, it is possible to obtain IPC with a predetermined hydrophobic and hydrophilic region. The same areas are present on the surface of soil aggregates, which can interact with IPC. It is important that polycomplexes are effective optimizers of shoots and shoots of plants, due to the presence of hydrophobic and hydrophilic sites in their chain.

One of the most important tasks in agriculture is the creation of waterproof aggregates of soils. The soil, which has no water-resistant structure, is prone to styling, occluding, crusting and is highly prone to erosion processes. The polyelectrolyte complexes proposed to date for use as soil fixers or soil formers are insoluble, which creates technological difficulties in their application. In addition, these polycomplexes are expensive and inaccessible. Solutions of such polycomplexes on the surface of soils must be applied sequentially or simultaneously from two containers. This creates technological difficulties associated with the uniform distribution of components on the soil surface, as a result of which it is difficult to obtain a homogeneous, stably strong soil-polycomplex crust.

The new multicomponent CMC - urea-formaldehyde resin (UFR) product offered by us for wide application due to its solubility in neutral and slightly alkaline media and long-term stability of solutions during storage makes it possible to prepare solutions containing both UFR and CMC in one tank. In addition, IPC can be obtained also in dry form (in the form of a powder), which dissolves well in water and is convenient for storage and transportation. Before application to the soil to increase the water resistance of the CMC-UFR film, the pH of the solution is reduced to 2.5-3, and then a water-insoluble IPC is formed on the soil. From a practical point of view, the application of the IPC CMC-UFR in agriculture and water management is of great importance, since polycomplexes have a major advantage over any known polymers because of their high anchoring abilities. There appears both technological and economic utility of their use for solving a number of agro-physical problems.

The large-tonnage of the initial components of the interpolymer



complex CMC-UFR and its solubility in water made it possible to apply it on a wide production scale [122,289,297].

For preparation of large-capacity solutions of IPC, a reactor with a stirrer or an industrial unit AZM-08 (reactor type), intended for preparation of high-dispersion emulsions (Fig. 4.6) [289] is proposed.

**A) Application of IPC for salt and dust suppression on the soil surface.**

Stability of IPC solutions and products within wide pH range of the medium (pH = 2-10) made it possible to apply them with great success as fixing agents of disperse systems in various regions of the country from the Aral Sea to Chernobyl. Disperse systems were tested with sandy loam and sand with the content of salts from the dried bottom of the Aral Sea. The results of the study of the effect of surface treatment of various soils with a 3% aqueous solution of IPC CMC - UFR at a rate of 10 g/m$^2$ on their water resistance are presented in Table. 4.5.

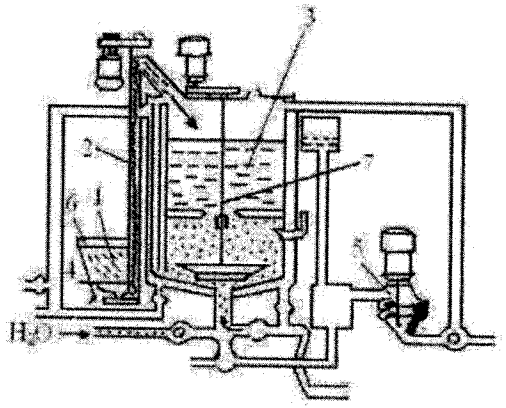



*Fig. 4.6. Scheme of the unit AZM-0,8: 1- receiving hopper; 2-vertical auger; 3-inner case of the unit; 4-mixer of the receiving hopper; 5-pump emulsifier; 6-grid; 7-mixer.*

Table 4.5.

**Influence of surface treatment of IPC CMC-UFR (10 g/m$^2$) on water resistance of various disperse systems**

| Type of soil | Treatment Soil with solution CMC + CFLTR | Water resistance of soil containing fractions of different dispersity,% | | |
|---|---|---|---|---|
| | | 1mm | 1-0,25 mm | The amount of fractions 0,25 mm |
| Sandy loam from the dried bottom of the Aral Sea | Processed | 6,3 | 28,1 | 34,4 |
| Sandy loam from the dried bottom of the Aral | not processed | 0,7 | 3,0 | 3,7 |
| Sand from Kok-Dara | processed | 50,1 | 25,0 | 75,1 |
| Sand from Kok-Dara | not processed | 0,7 | 18,7 | 19,4 |

As can be seen from Table 4.5, treatment with 3% solution of IPC mixtures and sand leads to an increase in the water resistance of these systems by 4-10 times, and the higher the dispersity of the soil, the greater the effect of processing it with a polycomplex. In addition, when treating old irrigated soils with IPC solutions, their flushing decreases by more than 80 times, i.e. if the washout in the treated areas was 0.08 t/ha, then in the control section - 7.2 t/ha. Hence, one can draw a conclusion about the advisability of using IPC in combating water and wind erosion, especially in areas subjected to erosion processes.

Field industrial tests for assessing the possibility of using a multicompartment based on CMC-UFR (MT-1) as a salt-dust suppressing agent were carried out in the South of the Aral Sea region - the South-eastern Prikizylkum southern prefabricated and Southwestern Priust-Urt drained parts of the sea.

3% MT-1 solution was applied to the flat surface of the barkhan (section 2) using a RDP-type atomizer (IDK-1) with a flow rate of 0.25; 0.5; 1.0 and 1.5 l /m$^2$. 3 hours after the treatment of the soil, a gusty wind > 10 m/s, which lasted for 6 hours, began.

During the tests an organoleptic assessment of the state of the



protective polymeric soil crust layer formed during the interaction of the soil and the interpolymer complex formed after application of the solution to the soil was carried out. The solidity values of the strength of the protective layer were measured and the value of the dust transfer from the treated and untreated surfaces in the aerodynamic installation was determined.

On visual inspection, it was noted that a polymer-soil layer 3 mm thick formed at the soil surface 0.5-1 hour at a solution flow rate of 0.25 l/m$^2$ and 7 mm at a solution consumption of 1.5 l / m$^2$. Survey of the site a day after treatment showed that a protective polymeric soil layer was preserved on the treated surface while the sand removal from adjacent untreated sections amounted to a height of 30 cm. The results of measurements of the mechanical strength of the protective polymeric soil crust layer are given in Table 4.6. The maximum measuring limit of the instrument was 5 kgs/cm$^2$.

Table 4.6

**Strength of the polymer-soil layer**

| Consumption of IPC solution, l / m$^2$ | Mechanical strength, kg/cm$^2$ | |
|---|---|---|
| | Smooth | Barkhan |
| 0,25 | 0,5 | 0,4-0,5 |
| 0,5 | 3,5 | 3-3,5 |
| 1,0 | more than 5 | more than 5 |
| 1,5 | more than 5 | more than 5 |
| control with water treatment (1 l / m2) | less than 0.1 | less than 0.1 |

Qualitative and quantitative assessment of the stability of salt-bearing soil to water-wind erosion during the application of the MT-1 solution showed the formation of a stable protective polymeric soil cover on the surface of the exposed bottom of the Aral Sea. The optimum ratio of the components of the formulation (CMC:UFR = 1:1) and flow rates of 1 l/m$^2$ is ascertained. The thickness of the polymer-soil crust layer is 5-6 mm, the mechanical strength of the layer is more than 5 kgs/cm$^2$.

**B) Application of IPC for dust suppression and localization radionuclides on the surface of soils**

Studies of the effectiveness of IPC for dust suppression and localization of radionuclides on the soil surface in the exclusion zone of the Chernobyl nuclear power plant have shown that MT-1 meets the requirements. In the course of the tests, aerosol activity in the air stream was measured over the experimental samples of the soil. Soil samples were exposed to air flow at a speed of 10.0 m/s in the aerodynamic unit AU-3. Soil samples were taken before and after treatment with a solution of the experimental site of the terrain, and also after treatment of the formed protective layer with water. By changing the specific activity of aerosols over soil samples, a conclusion was made about the effectiveness of MT-1 for dust suppression.

The tests were carried out on the site located in the area of Yanovsky dachas on the "Western Trail", 5 km from the Chernobyl NES, azimuth 250. Characteristics of the site: the first under the floodplain terrace of the Pripyat River, dry, composed of thick sands, with soddy-weakly podzolic sandy soils. The gamma background on the surface of the soil is 7-9 millicrustntgen per hour, the density of contamination with gamma radionuclides is 2500-3200 CI / $KM^2$. The experimental site is a flat area, devoid of vegetation, an area of 0.2 hectares. The site is located at a distance of 1000m from the road Pripyat - Chistogalovka.

A 3% solution of MT-1 was applied to dry sandy soil at an air temperature of + 30°C and a relative humidity of 60%. To apply the mortar to the ground, a special APC-14 machine was used, equipped with a slotted nozzle DN-3 from behind. The viscosity of the MT-1 solution is close to the viscosity of water, so there was no difficulty in spraying it through the DN-3 nozzle. During the tests, it was noted that APC-14 at a speed of 5 km/h allows achieving a solution flow rate of 0.75 l /$m^2$. The width of the treated strip is 3.0 m. However, the quality of the treatment area is low due to uneven coverage and insufficient solution for wetting dry ground. Repeated treatment makes it possible to obtain a polymer-soil crust layer 4-6 mm thick.

To assess the effectiveness of the dust cover, the aerosol lift and radioactive contamination of the air above the soil samples taken at the test site before and after treatment with the solution were measured at an air flow rate of 10 m/s. A sample of loose soil is an active source of radioactive air pollution. The results of measuring the specific activity of the aerosol in the air flow are given in Table 4.7.



Table 4.7.

**Results of specific aerosol activity measurement in the flow of air above the samples**

| Activity before treatment $10^{-6}$ CI / M | | Activity after treatment $10^{-6}$ CI / M3 |
|---|---|---|
| 4,87 | | 0,1 |
| 37,5 | | 3,2 |
| 97,6 | | 6,5 |
| 56,4 | | 1,3 |
| 179,3 | | 4,1 |
| Average value for the plot | $75*10^{-6}$ | $3,7*10^{-6}$ |

The data show that the use of the proposed MT-1 multicompartment allowed to reduce the aerosol activity in the air flow over the soil samples by an average of 20 times (from 10 to 48 times).

The protective polymeric soil crust layer was treated with water in an amount of 100ml / $cm^2$, dried and tested in an aerodynamic installation at an air flow velocity of 10.0 m/s. The change in the magnitude of the rise of radioactive substances and aerosols from the surface of the protective layer did not exceed the value of the measurement accuracy (16% of the measured value), which indicates the resistance of the protective layer to atmospheric precipitation.

Determination of the mechanical strength in the field conditions showed that the strength of the protective crust layer at the consumption of the solution 0.75 l/$m^2$ was, on the average of 7 measurements, 3.5 kgf/$cm^2$, and at a flow rate of 1.5 l /$m^2$ exceeded 5.0 kgs/$cm^2$ (measurement limit of the device).

A monolayer of sand, fixed by a polymer layer on the concrete surface, is not displaced by horizontal action with a force of up to 5 kgs /$cm^2$.

Based on the tests, the following conclusions are made:

1. The method for estimating the effectiveness of dust suppression and localization of radionuclides on the soil surface is verified and meets the requirements.

2. Interpolymeric complex based on carboxymethyl cellulose and urea-formaldehyde resin (MT-1) is an effective dust suppressant in a

section of terrain that is not subjected to mechanical stress. The use of MT-1 allows an average of 20 times to reduce the transport of radioactive substances at an air flow rate of up to 10 m/s.

3. The mechanical strength of the protective polymeric soil crust layer at the expense of a 3% solution of 0.75 l /$m^2$ is 3.5 kgf /$cm^2$ on an average, and exceeds 1.5 kg/$cm^2$ at a flow rate of 1.5 l /$m^2$.

4. The solution was prepared by using any vessel equipped with a stirrer and sprayed from available technical means, for example, APC-14. However, in order to obtain a more uniform and effective coating, it is necessary to use special means for applying the solution.

5. If necessary, the solution can also be used to fix radioactive substances on the surface of concrete and brick.

6. Testing the reliability of the protective polymeric soil layer for 13 months showed that it is resistant to the effects of atmospheric precipitation, during which time more than 600 mm of rain fell.

7. Based on the tests carried out and the experience of using the MT-1 polycomplex in the agriculture of the Republic of Uzbekistan, it is possible to recommend the use of the tested MT-1 poly-complex to prevent wind erosion of soils contaminated with radioactive substances.

### 4.7. Application of IPC in cotton growing

As mentioned above, polycomplexes are new effective soil structureers and mulch material. The systems we studied were selected for the purpose of their application in agriculture and water management for the improvement of soil characteristics. In this connection, such components as polyanion-carboxymethyl cellulose and amine-containing oligomers and polymers playing the role of polycation widely used in industry were selected. Each component alone has long been used in the national economy. The use of each component separately in agriculture has a number of drawbacks, such as the water resistance of CMCs as a structurant, and UFR, as a three-dimensional, insoluble polymer that does not dissolve in any solvent, forms a homogeneous film.

The obtained polycomplex films based on CMC-UFR and CMC with other amine-containing oligomers possess unique physicochemical properties, such as stability over a wide range of pH of the medium, inhibition by sufficiently high deformation-strength, sorption, ultrafiltration properties. These properties make it possible to widely use films in agriculture, in particular, in cotton growing. They are environmentally friendly and economically viable [298].



**Application of IPC to prevent cortex formation of soils.**

In 1990-2005, we conducted laboratory and production tests on the use of IPC in cotton growing to improve the agrophysical characteristics of soils, to prevent soil crust formation in order to obtain guaranteed seedlings regardless of the weather conditions, and to increase crop yields.

Preventing soil cortex formation is important for obtaining ample guaranteed cotton seedlings and a high yield. For example, the spring and summer of 1997 were unusually rainy. According to the data of the Hydrometeorological Center of the Republic of Uzbekistan in the spring period from March to May, months from 92 days 49 were rainy. Because of frequent rains and showers, there was a significant erosion of the soil in the furrows, followed by cortex formation on them under the action of the sun. Because of the crust, it was necessary to resettle cotton (excluding other crops) on an area of 400 thousand hectares, i.e. the fifth part of all areas of cotton fields of the republic (1.9 million hectares). Particularly affected Fergana region, where in many fields, the resettlement was carried out twice, and in a number of districts and three times.

The economic losses from soil cortex formation are great. Only in the Fergana region they are estimated at tens of millions of soums a year. In the collective farm named after H.Tursunkulov in 1997 in brigades № 11 and 12 in serozem soils, the CMC-UFR-soot (MT-2) multicomplex proposed by us was tested in order to protect cotton seedlings from wind and water erosion and to prevent the formation of soil crust. The test results showed that uniform shoots were obtained in the experimental sites, despite unfavorable critical weather conditions, and in the control areas cotton was crossed three times.

Serozem soils are prone to occluding during rains and the formation of a powerful, up to 4-5 cm, soil crust as a result of the drying out of the upper soil layer exposed to rain drops. The soil crust exerts a depressing effect on seedlings, the emergence of shoots and the development of young plants, the thickness of the soil crust depends on the amount of precipitation, rain intensity, physical-mechanical and chemical properties of soil aggregates. Known methods of preventing and preventing soil crust formation, such as mechanical loosening and the introduction of mulch stock, are not effective enough. For example, mechanical loosening by a rotary hoe is possible only before the emergence of seedlings and only when heavy rains do not follow after it. Preventing crust formation by ketting hoe requires very much manual labor and time.

The surface treatment of the soil with an IPC solution was carried out with a belt, 10-15 cm width above the sowing line, simultaneously with sowing the cotton seed in Fig. 4.7. The results of the study of the

application of various IPC in cotton growing are given in Table. 4.8. It can be seen that all the IPC studied are effective in counteracting soil crust formation, which help to reduce the thickness of the crust several times, as a result of which the germination of cotton seeds increases.

Table 4.8

**A summary table of data on the thickness of the soil crust in April-May months in large-scale field experiments**

| Year | Experimental site location | Option of experience | Width of soil crust, mm |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 1997 | Uchkhoz TIIM | Control | 11,3 |
| | | PAC-ПЭИ | 4,5 |
| | | K-4 | 6,1 |
| 1998 | Uchkhoz TIIM | Control | 6,3 |
| | | PAC -PEI | 2,6 |
| | | K-4 | 3,1 |
| 1999 | Uz RCI | Control | 30,2 |
| | | CMC-UFR | 10,7 |
| | | K-4-ДЭАЭМА | 10,4 |
| 2000 | Uz RCI | Control | 11,9 |
| | | CMC-UFR | 4,3 |
| | | K-4-DCG-GM | 6,4 |
| 2001 | Uz RCI | Control | 23,0 |
| | | CMC-UFR- carbon- | 13,4 |
| | | K-4-DCG-GM | 13,0 |
| 1999 | Uchkhoz TIIM | Control | 25-30 |
| | | CMC-UFR | 8-10 |
| | | CMC-UFR - carbon- | 15 |
| 2002 | Uz RCI | CMC- PMAG | 4 |
| | | CMC-UFR | 2,5 |
| | | Control | 25 |
| 2003 | Uz RCI | CMC-UFR | 5 |
| | | CMC-PMAG | 5 |
| | | CMC-DCG-GM | 6 |
| | | Control | 35 |

In order to study the effect of soil treatment by different IPCs on seed germination and cotton growth, the stability of the formed polycomplex-soil crust during the interaction of atmospheric precipitation was carried out



in Vagner's vessels and small-scale experiments in the field.

The results of studies on the effect of soil treatment by polycomplexes on the germination of cotton seeds in small-scale experiments are presented in table 4.9.

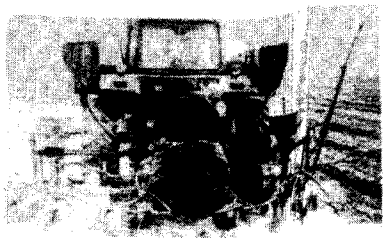


*Fig. 4.7. Application of a solution of an interpolymer complex*

Table 4.9

**Influence of IPC on the germination and development of cotton Effect of soil treatment by polycomplexes on the germination of cotton seeds**

| Variant | Germination | | | | | |
|---|---|---|---|---|---|---|
| 1 | 2 | | | | | |
| | 1997 | | | | | |
| Date | 19.04 | 24.04 | 25.04 | 27.04 | 29.04 | 04.05 |
| Control | seeding | 0 | 8,2 | 45,3 | 70,8 | 75.5 |
| PAC-PEI | seeding | 5,4 | 23,9 | 62,9 | 74,7 | 88.2 |
| K-4 | seeding | 6,1 | 23,4 | 58,4 | 73,7 | 88,1 |
| | 1998 | | | | | |
| Date | 13.04 | 22.04 | 25.04 | 29.04 | | |
| Control | seeding | 37,4 | 42,8 | 80,5 | | |
| PAC-PEI | seeding | 39,4 | 48,6 | 93,0 | | |
| K-4 | seeding | 37,4 | 48,3 | 93,0 | | |
| | 1999 | | | | | |

| Date | 30.03 | 05.04 | 15.04 | 21.04 | | |
|---|---|---|---|---|---|---|
| Control | seeding | 101 | 15 | 40 | | |
| CMC-UFR | seeding | 31 | 60 | 75 | | |
| | 2000 | | | | | |
| Date | 13.04 | 22.04 | 30.04 | 05.05 | 10.05 | |
| Control | seeding | 25 | 30 | 45 | 50 | |
| CMC-UFR | seeding | 30 | 50 | 72 | 75 | |
| K-4-DCG-GM | seeding | 40 | 50 | 78 | 80 | |
| | 2001 | | | | | |
| date | 19.04 | 29.04 | 02.05 | 05.05 | | |
| Control | seeding | 57 | 65 | 81 | | |
| CMC-UFR | seeding | 72 | 83,7 | 96 | | |
| K-4 | seeding | 72 | 86 | 93 | | |

It can be seen that in 1997, the total germination in the control was 75.5%, and in the experimental plots - 88.1%. In 1998 in the control the total germination was 80.5%, in the experiment-93.02%. In the following years, there was also an increase in the germination of cotton seeds by 15-20% compared with the control. In addition, in the experimental plots, shoots appear 1-2 days earlier than in the control plots.

Thus, cultivation of soils by polycomplexes creates optimal agro-soil conditions for the development of seedlings. In case of heavy rains, the water was filtered through the IPC well enough, there was no overmoistening, and with prolonged withering in a little rainy spring, the moisture was kept much longer at a level sufficient for plants, which justifies the increase in the germination of cotton seeds.

### 4.8. Vegetational, small-scale and field tests of IPC in cotton growing

**a) Vegetation and small-scale tests.**

To fully identify the method of applying IPC on the agrophysical conditions of germination of seeds, we conducted vegetation experiments with cotton. In these experiments, by mixing, complete soil homogeneity is



achieved in all the vessels and the same necessary moisture and nutrient regime are maintained.

Experiments on the use of interpolymer complexes CMC-UFR, CMC-PMAG and CMC-UFR with soot filler were carried out according to the method of Uz RCI. Methods of applying IPC ranged from surface application to processing the entire volume of soil (0-30 cm). The experiments were repeated four times.

The account of cotton seedlings was conducted every day after their appearance in all experiments before thinning. The data obtained and generalized in the survey of shoots and the results of phenological observations are given in Tables 4.10 (1998 data) and 4.11 (1999 data).

Observations showed that shoots in variants of the experiment using IPC appeared one day earlier in comparison with the control. The most optimal option was the treatment of soil with an IPC solution, where the surface (0-5 cm) soil layer was structured (Tables 4.10, 4.11).

Acceleration of growth and development of cotton in the vegetation experiments of 1998 and 1999 with the use of IPC affected the accumulation of fruit elements. The strong growth and intensified rates of development of cotton in options with the use of IPC in the initial period contributed to a relatively greater accumulation of fruit elements and their earlier maturation - from 2 to 5-6 days in 1998 and 1999, respectively. In this connection, in the IPC options, the raw cotton crop was collected, mainly due to the first and second harvest, and on the control - due to the second and third.

From the data presented in Table 4.10 and 4.11, we can draw the following conclusion. By structuring the soil layer with IPC, it is possible to achieve an increase in cotton yields, which is clearly seen in the increase in yields in the experimental variants by 20-40% in 1998 and by 20-30% in 1999. For the whole vegetation period irrigation water was supplied by definition the moisture deficit, which was determined by weighing. The moisture content of the soil was maintained according to the scheme of 70-80-60% of the PPV.

Experimental data allow us to conclude that the application of IPC leads to a decrease in evaporation of moisture, since the moisture reserve in the soil is preserved due to the structuring of the IPC soil with the formation of a polycomplex-soil crust.

When treated with an IPC solution, the soil does not agitate and silt, as in the control variants, the water penetrates into the soil evenly. Surface treatment of soils retained the looseness of the soils during watering, which led to a decrease in the flow of moisture compared to the control (Table 4.10, 4.11)

Thus, the results of vegetation experiments confirmed the undoubted effectiveness of soil treatment by polycomplexes both superficially and volumetrically, in order to increase cotton yield and improve the water regime of meadow and serozem soils.

**b) Field testing of IPC in cotton growing**

The processing of soils by polycomplexes creates optimal conditions for plant life, beginning with the early development of seedlings. After heavy spring rains in the fields an empty spot without shoots is formed, the emergence of seedlings emerges due to rotting of seeds or crust formation on the surface of soils. The polycomplex soil film formed during the soil treatment with an IPC solution raises the temperature on the soil surface and keeps the soil moisture in the optimal regime. On elevations in the field, the film does not allow moisture to quickly evaporate, and during heavy rains contributes to the rapid drainage of rainwater sideways from the seedlings to the interrow rows. The soil structure contributes to faster water retreat into the horizon. This eliminates the closure of seeds, sprouts, and the formation of soil crust. Field production experiments using IPC have been carried out, beginning in 1998, in various cotton-growing regions of the republic on an area from one to three hundred hectares. In all experiments positive effects of the effect of IPC treatment on the germination, growth, development and yield of cotton were observed.

As the large-scale and production multi-year experiments of 1998-2005 show, on the basis of "UzRCI", in Uchkhoz TIIM and in some cotton-growing farms of Uzbekistan, the full germination of seeds in the fields treated with polycomplex is 17% higher than in control ones. So that there would be no crop losses, seeds were planted in empty places on the field. After thinning, the density of plant standing in the control and experiment was normal, but on the experimental plot an average of 5,000 / ha more. The severity and neglect in the experimental plots, thus, was reduced to a minimum.

Phenological observations for: the results of the experiment on the effects of IPC on plant development and yields were evaluated in accordance with the requirements for setting up experimental work in cotton growing [279].

Thus, the use of IPC in cotton growing creates favorable agrophysical conditions for the growth of cotton in the spring, ensuring uniform and normal germination of seeds, the density of plant standing, increasing the accumulation of capsules by 0.5 pcs. -4- per 1 plant and the weight of the raw material per box by 5-6% compared to the control, which leads to an increase in the yield of cotton by 3-6 t / ha (Table 4.12).



**Phenological data of vegetative experiments with IPC, the year of 1998 (average data from 4 reruns)**
(soil - meadow)

| № | Experiment variant | Germination, % | Height of the main stem, cm per 1.09 | Number of days from seeding to the beginning. | | Crop of raw cotton per 1 plant, g | Addition of crop to control, % | Water consumption per 1g of raw-cotton, l |
|---|---|---|---|---|---|---|---|---|
| | | | | Budding | Flowering | | | |
| 1 | Soil+11-7g; P2O5 – 6g; $K_2O$ – 4g - BACKGROUND | 75 | 74,0 | 35 | 61 | 27,4 | | 4,5 |
| 2 | BACKGROUND+CMC-UFR 0,02 % of soil mass on the whole layer | 80 | 73,5 | 33 | 59 | 38,9 | 41,9 | 3,1 |
| 3 | BACKGROUND+CMC-UFR 0,02 % of soil mass on the whole layer 0-15cm | 90 | 81,0 | 33 | 58 | 36,8 | 34,3 | 3,3 |
| 4 | BACKGROUND+CMC-UFR 0,02 % of soil mass on the whole layer 0-5cm | 98 | 81,0 | 31 | 57 | 39,9 | 45,6 | 3,0 |
| 5 | BACKGROUND+CMC-UFR 0,02 % spraying of the soil from the surface (30 mcm film thickness) | 83 | 79,8 | 33 | 57 | 41,2 | 50,4 | 3,0 |
| 6 | BACKGROUND+CMC-PMAG 0,02 % of soil mass on the whole layer | 88 | 83,0 | 32 | 59 | 34,6 | 26,2 | 3,2 |
| 7 | BACKGROUND+ CMC-PMAG 0,02 % of soil mass on the whole layer 0- 15cm | 93 | 79,3 | 33 | 58 | 39,8 | 45,3 | 2,9 |
| 8 | BACKGROUND+ CMC-PMAG 0,02 % of soil mass on the whole layer 0- 5cm | 95 | 83,7 | 32 | 57 | 40,2 | 46,7 | 3,0 |
| 9 | BACKGROUND+CMC-PMAG 0,02 % spraying of the soil from the surface with 2%-IPC solution | 85 | 86,0 | 32 | 57 | 40,7 | 48,5 | 2,9 |

Table 4.11

**Phenological data of vegetative experiments with IPC, the year of 1999 (average data from 4 reruns)**

**(soil – typical serozem)**

| № | Experiment variant | Germination % | Height of the main stem, per 15,08cm | Number of days from seeding to the beginning | | Crop of raw cotton per 1 plant, g | Addition of crop to control, % | Water consumption per 1g of raw-cotton, l |
|---|---|---|---|---|---|---|---|---|
| | | | | Budding | Flowering | | | |
| 1 | Soil+11-7g; P2O5— 6 g; K2O - 4 g. - BACKGROUND | 75 | 80,6 | 33 | 65 | 54,9 | - | 2,61 |
| 2 | BACKGROUND+CMC-UFR 0,02 % of soil mass on the whole layer | 78 | 85,8 | 31 | 62 | 56,0 | 2 | 2,56 |
| 3 | BACKGROUND+CMC-UFR 0,02 % of soil mass on the whole layer 0-15cm | 93 | 85,0 | 30 | 63 | 60,9 | 11 | 2,32 |
| 4 | BACKGROUND+CMC-UFR 0,02 % of soil mass on the whole layer 0-5cm | 97 | 85,0 | 29 | 61 | 63,3 | 15 | 2,22 |
| 5 | BACKGROUND+CMC-UFR 0,02% spraying of the soil from the surface | 80 | 84,0 | 31 | 63 | 65,3 | 19 | 2,15 |
| 6 | BACKGROUND+CMC-PMAG 0,02 % of soil mass on the whole layer 0-30cm | 93 | 80,0 | 30 | 60 | 69.1 | 26 | 2,06 |
| 7 | BACKGROUND+ CMC-PMAG 0,02 % of soil mass on the layer 0-15cm | 93 | 89,3 | 30 | 60 | 69,6 | 27 | 2,03 |
| 8 | BACKGROUND+ CMC-PMAG 0,02 % of soil mass on the whole layer 0-5cm | 95 | 85,5 | 29 | 59 | 69,3 | 26 | 2,03 |
| 9 | BACKGROUND+CMC-UFR (carbon-black) 0,02 % of soil mass on the layer 0-5cm | 95 | 91,2 | 30 | 61 | 70,1 | 28 | 2,00 |
| 10 | BACKGROUND+CMC-UFR (carbon-black) 2% spraying of the soil on the surface | 95 | 83,0 | 29 | 60 | 71,2 | 30 | 1,98 |



Table 4.12

**The results of production tests of the influence of IPC on the yield of cotton**

| Tested preparation | Years | Site of experiment | Area, ha | Crop capacity, c/ha | | |
|---|---|---|---|---|---|---|
| | | | | E | C | A |
| PAC-PEI | 1998 | Uchkhoz TIIM | 1 | 34,5 | 30,0 | 4,5 |
| K-4 | 1998 | Uchkhoz TIIM | 1 | 32,0 | 30,0 | 2,0 |
| PAC-PEI | 1999 | Uchkhoz TIIM | 2 | 44,7 | 38,5 | 6,2 |
| CMC-UFR | 1999 | Uchkhoz TIIM | 1 | 31,8 | 27,5 | 4,3 |
| CMC-UFR | 2000 | UzRCI | 0,4 | 32,0 | 26,9 | 5,1 |
| CMC-UFR | 2000 | Uchkhoz TIIM | 5 | 31,7 | 27,4 | 4,3 |
| CMC-UFR | 2001 | Uchkhoz TIIM | 2 | 37,6 | 34,0 | 3,6 |
| CMC-UFR | 2001 | Uchkhoz TIIM | 10 | 32,8 | 25,6 | 4,6 |
| CMC-UFR | 2001 | c-f «Tinchlik» | 2 | 40,8 | 36,5 | 4,2 |
| CMC-UFR | 2002 | Uchkhoz TIIM | 50 | 29,8 | 26,3 | 3,5 |
| CMC-UFR | 2002 | c-f «Tinchlik» | 16 | 37,5 | 32,8 | 4,7 |
| CMC-UFR | 2002 | c-f «Kim-Pen-Khwa» | 20 | 31,0 | 28,0 | 3,0 |
| CMC-UFR+(carbon black) | 2003 | Farm «Omad» | 1 | 38,0 | 32,7 | 5,8 |
| CMC-UFR | 2003 | Farm «Omad» | 1 | 37,2 | 32,7 | 4,5 |
| CMC-UFR+(carbon black) | 2003 | Uchkhoz TIIM | 6 | 34,0 | 28,0 | 6,0 |
| CMC-UFR | 2003 | Uchkhoz TIIM | 10 | 32,0 | 28,0 | 4,0 |
| CMC-UFR+(carbon black) | 2004 | c-f «Kim-Pen-Khwa» | 0,5 | 34,8 | 28,4 | 6,4 |
| CMC-UFR | 2004 | c-f «Kim-Pen-Khwa» | 0,5 | 32,7 | 28,4 | 4,3 |
| CMC-UFR+(carbon black) | 2005 | Farm «Omad» | 5 | 36,8 | 31,6 | 5,2 |
| CMC-UFR | 2 | Farm «Omad» | 5 | 39,6 | 35,2 | 4,4 |
| CMC-PMAG | 2 | Farm «Omad» | 2 | 30,9 | 26,4 | 4,5 |
| CMC+UFR+(carbon-black) | 2 | Uchkhoz TIIM | 5 | 31,2 | 26,4 | 4,8 |

### 4.9. Influence of IPC on agrophysical properties of soils

In the previous sections, we demonstrated the specific properties of the IPC, resulting from the polymer structure and the nature of the reagents. The available results of the investigation of the physicochemical and mechanical properties of IPC indicate the possibility of regulating the nature of the surface of soil particles, the structural-sorption and structural-mechanical properties of soil dispersions, and, consequently, the creation of a system with predetermined properties.

It follows from the foregoing that the regulation of the agrophysical properties of soils is based on a directed change in the processes of interchain interactions between the components of the IPC, and therefore between the dispersed phase and the IPC. One way of this regulation is the use of IPC with certain hydrophilic and hydrophobic areas, which in turn depend on the nature, complementarity and flexibility of the initial components of the IPC. The hydrophilicity of IPC depends on the charge density on the oligomer chain, the ratio of the interacting components and the structure of the IPC.

In this regard, we have before us the task of determining the influence of IPC on the agrophysical properties of soils, depending on the application of IPC to the soil surface or in volume, and also the possibility of its regulation. One of the solutions to the problem of improving the agrophysical conditions of soils is the creation of waterproof aggregates of soils.

The water resistance of the macrostructure of soils treated with IPC solutions was studied on soil aggregates with a diameter d = 2-3.3-5 mm and in undivided soil with a surface treatment of IPC.

The results of laboratory experiments are presented in Table 4.13.

Table 4.13.

**Influence of IPC on water resistance of soil aggregates with a diameter of 5 mm**

| | Type of interpolymer complex | | | | | | |
|---|---|---|---|---|---|---|---|
| | CMC-PEI | PAC-PEI | PAC-DMDAA | CMC-UFR | K-4-PEI | K-4 | Control |
| Number of breaking drops (Vilensky method) | 1700 | 1282 | 1112 | 991 | 1560 | 984 | 12 |



The water resistance of serozem soil aggregates was compared with sizes 1-2, 2-3, 3-5, 5-7 mm and similar aggregates treated with such a dose of polycomplex, which is equivalent to applying it to the soil surface with a thickness of 15 μm (7-7.5 g /m$^2$). Accurate measurement of the thickness of the film on aggregates is complicated by the fact that some of the solutions of the components are sorbed by the internal parts of the aggregates. In this regard, for a qualitative assessment of the water resistance of aggregates on the surface of the soil, they imparted 7.5 g/m$^2$ on the basis of the dry matter of CMC and UFR.

The water resistance of control samples of typical long-period irrigation sierozems ranges from 5.5 to 6.8%, in meadow soils of the Srednechirchik district of the Tashkent region - from 5.3 to 5.6%. The water resistance of soil aggregates filled with polycomplexes for the same soils is 95%.

After drying during a second test, the water resistance of aggregates treated with IPC soils was 91-92%. After three-time testing of soil aggregates treated with PC, water resistance is not significantly reduced - up to 86-89%. Treatment of aggregates of serozem soils with water-soluble polymers from the "K" series with a dose of 0.2% to the soil mass increases their water resistance to 75%, and for polycomplexes - up to 89% against 8% in the control.

Thus, it can be seen from the foregoing that after processing with polycomplexes, the water resistance of soil aggregates is higher than when treated with one of its components or with polymers from the "K" series. This means that the IPC dose for soil cultivation with the purpose of fixing it to achieve the same effect is lower, which is of great practical importance.

As the results of laboratory studies show, the water resistance of soil aggregates treated with polycomplexes (Table 4.13) of CMC-PEI and K-4-PEI is of the greatest importance.

However, the constituent components of these IPCs (PAC, PEI) are expensive and inaccessible. Therefore, polymer complexes based on CMC and amine-containing oligomers and polymers proved to be optimal for the solution of the problem.

IPC solutions based on CMC and UFR were applied to the soil surface from 0.5 to 1% of its mass. The soil crust, which was structured by polycomplexes, was 0-1 cm thick and subjected to waterproofing, microaggregate and mechanical composition.

From the data given, it can be seen that the treatment of soils with solutions of CMC-UFR and CMC-PGMG polycomplexes increases its water resistance tens of times (Table 4.14) [122, 136]. By changing the

composition of the interacting components, i.e. the change in the ratio of hydrophobic and hydrophilic regions in the structure of the polycomplex, it is possible to increase its structure-forming properties due to free functional groups of macromolecules. Treatment with individual polycations of UFR and PGMG results in an insignificant increase in water resistance of soils, and a small addition of CMC in their composition increases the structure-forming properties. It should be noted that the CMC system with urea-formaldehyde oligomers has an undeniable advantage over other IPC. The components of this system (CMC and UFR) are large-tonnage, because of the low charge density of the IPC, it is possible to obtain their solutions in one common solvent and apply to the soil from one container. It is possible to obtain a soluble "semi-finished" IPC, which is stable for a long time (more than 2-4 years), this creates great technological convenience.

Table 4.14.

**Effect of IPC on the water resistance of serozem soils**

| Experiment Variant | Fraction mass, % | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 1-0,25 | 0,25-0,05 | 0,05-0,01 | Sum of fractions | |
| | | | | | 0,01 | 0,25 |
| Control | 0,9 | 2,3 | 44 | 47,9 | 4,4 | 3,2 |
| CMC-UFR | | | | | | |
| 1:0 | 8,70 | | | | | 46,4 |
| 1:1 | 67,6 | 11,3 | 10,9 | 7,5 | 2,7 | 78,9 |
| 4:1 | 63,2 | 18,6 | 12,6 | 4.0 | 1,6 | 81,8 |
| 1:4 | 45,7 | 31,9 | 16,0 | 3,6 | 2,8 | 77,6 |
| 0:1 | - | - | - | - | - | 15 |
| CMC-PHMG | | | | | | |
| 1:1 | 34.1 | 31,2 | 22,47 | 8,6 | 3,6 | 65,2 |
| 4:1 | 40,9 | 30,9 | 21,7 | 6,2 | 3.1 | 71,8 |
| 1:4 | 13,8 | 26,17 | 42,5 | 14,3 | 3,3 | 39,9 |
| PHMG | - | - | - | - | - | 10 |
| CMC-CFLT | 29,6 | 38,2 | 23,1 | 6,4 | 2,6 | 67,8 |
| CMC -PMAG | 14,8 | 33,8 | 38,2 | 10,3 | 2,8 | 48,6 |
| CMC -DCG-GM | 5,6 | 36,5 | 42,6 | 12,5 | 2,8 | 42,1 |

The results of the study of ultrafiltration, sorption properties and swelling of IPC films show that the polycomplex soil crust formed on the soil surface should improve the structural and absorbing properties, as well as the water and air permeability of the soil. The nature of the change in the value of the physico-mechanical properties of the IPC from the component ratio and the pH of the medium indicates a wide range of permissible loads



that IPC films can withstand under external influences.

The maximum structure-forming effect of different IPCs depends on the initial soil moisture. For systems with low charge density, for example, CMC-UFO, the maximum effect of structure formation is manifested when they are introduced into soil with a moisture content of 8%, and for systems with a high charge density (CMC-PMAG, CMC-PGMG, CMC-DHG-GM). The greatest structure-forming effect is observed when applied to the soil with a moisture content of 16-20%. This dependence, apparently, can be explained by the nature of the original components and the charge density of the IPC. A polymer complex of CMC with strong polycations (PMAG, PMGH, DHG-GM) is obtained by applying to the soil components at the same time from individual containers. Intensive interaction of the initial substances of the IPC occurs on the substrate (matrix) - on the surface of the soil. At the same time, the high humidity of the latter ensures a uniform distribution of the interacting components.

IPC CMC with urea-formaldehyde resins is applied to the soil surface in the form of a suspension from a single vessel, where the components are in interaction and therefore do not require high soil moisture. The application of IPC CMC-UFR to soil with a moisture content of 8% provides an optimal technology for obtaining a soil-polycomplex film.

The most important physical properties of soils, such as porosity, moisture capacity, water permeability depend on its mechanical composition, quantity of adhesives, etc. Investigation of the mechanical composition of soils treated with IPC indicates some partial consolidation of fractions 0.05-0.25 (fine sand), due to dust fractions (0.001-0.05) (Table 4.15). The computed values of the granulometric indicator of the soil structure [136] show that the treatment of IPC soils increases the potential ability of the soil to be structured (Tables 4.15, 4.16).

As it was shown above, the properties and structure of the IPC can be regulated by changing the ratio of the initial components and the conditions of the complex formation. Water resistance of soil aggregates treated with IPC reaches 90%, which is explained by the fact that the complexes function as a structure-forming and mulch material. For example, known polymeric structurizers of the "K" series, gluing aggregates of soils, interact with the crystals of minerals with hydrogen bonds between polar groups and oxygen of clay materials, as well as electrostatic forces between the ions of the dispersed particle and the functional groups of the polymer. When using polycomplex structurizers such interactions are minimized due to the formation of interpolymer bonds.

The introduction of IPC emulsions or solutions of interacting components leads to an increase in the content of this fraction (d> 0.25

mm) in the soil, which determines its macrostructural state. The change in the values of the microaggregate composition of soils treated with IPC (Table 4.15) indicates that polycomplexes, covering the soil surface, increase its water resistance, but along with it its microaggregate composition also improves. Here, too, the influence of the ionic forces of the original components is manifested. In the case of strong polyelectrolytes, soil aggregates with IPC interact only due to their defective areas. Therefore, in the processing of IPC soils formed by strong polyelectrolytes, the microaggregate and mechanical compositions vary little, since the IPC envelops the soil aggregates superficially and the interaction of the IPC with the soil aggregate occurs only on the surface of the latter. When treating IPC soils obtained from weak polyelectrolytes, the interaction of IPC with the soil matrix takes place both on the surface and in the volume of the soil.

In addition, the hydrophobic and hydrophilic soil sections present on the soil surface are partially bound to the functional groups of the interacting components of the IPC. This leads to a slight increase in the structural index (Table 4.14) and to a certain increase in the agronomically valuable fraction d = 0.1 mm (Table 4.16).

One of the most important factors for plant growth is the temperature of the environment and soil. Due to the increase in soil temperature under the influence of IPC, a number of heat-loving crops, in particular cotton, can be sown a few days earlier, and the shoots unhindered through the polycomplex-soil layer [122, 136].

IPC as an artificial structure-forming and mulch material of soil limits evaporation of soil moisture (Table 4.17) and, as a rule, reduces heat transfer. In this case, the soil temperature in spring and at all depths rises, and in summer the soil does not overheat due to the limitation of heat fluxes directed from the hot surface layer of air into the soil.



Table 4.15.

**The granulometric composition of soil treated with IPC in different ratios and concentrations**

| Experiment variant | Fraction mass, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0,25 | 0,25-0,1 | 0,1-0,005 | 0,05-0,001 | 0,01-0,005 | 0,005-0,001 | 0,001 | Physical clay | Indicator of structure (Pc) in % |
| Control | 0,5 | 0,87 | 5,7 | 52,6 | 13,16 | 15,28 | 12,75 | 41,19 | 15,7 |
| CMC:UFR | | | | | | | | | |
| 1:1 | 0,8 | 2,97 | 12,3 | 48,66 | 10,4 | 12,16 | 12,76 | 35,32 | 17,9 |
| 4:1 | 0,9 | 3,05 | 13,1 | 46,9 | 11,85 | 12,2 | 12,1 | 36,15 | 17,1 |
| 1:4 | 0,83 | 3,0 | 12,5 | 46,26 | 12,7 | 12,1 | 12,5 | 37,3 | 17,6 |
| CMC:CFLT | | | | | | | | | |
| 1 % | 0,4 | 0,8 | 11,0 | 48,7 | 11,6 | 13,6 | 12,9 | 38,1 | 17,5 |
| 2% | 0,65 | 0,9 | 10,5 | 48,5 | 12,45 | 14,05 | 12,9 | 39,4 | 17,2 |
| 3% | 0,6 | 0,9 | 10,6 | 48,85 | 13,35 | 13,35 | 12,35 | 39,05 | 16,4 |
| CMC: PMAG | | | | | | | | | |
| 1 % | 0,4 | 0,85 | 4,9 | 52,1 | 13,75 | 14,15 | 13,85 | 41,75 | 17,3 |
| 2% | 0,4 | 0,8 | 4,9 | 53,05 | 12,95 | 15,4 | 12,5 | 40,85 | 15,4 |
| CMC: DCG-GM | | | | | | | | | |
| 1 % | 0,45 | 0,75 | 12,05 | 50,0 | 11,65 | 13,1 | 12,0 | 36,75 | 16,1 |
| 2% | 0,9 | 1,15 | 9,7 | 47,9 | 14,2 | 14,75 | 11,4 | 40,35 | 14,8 |
| 3% | 0,7 | 1,2 | 2,8 | 54,7 | 14,35 | 13,35 | 12,5 | 40,2 | 15,2 |

Table 4.16

**Microaggregate composition of soil treated with IPC in different proportions and concentrations**

| Experiment variant | Fraction mass ,% | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0,25 | 0,25-0,1 | 0,1-0,05 | 0,05-0,01 | 0,01-0,005 | 0,005-0,001 | 0,001 | 0,1 |
| Control | 0,67 | 1,45 | 9,45 | 61,25 | 11,6 | 13,2 | 2,4 | 2,2 |
| CMC:UFR | | | | | | | | |
| 1:1 | 7,88 | 7,13 | 15,3 | 47,18 | 9,38 | 9,96 | 3,19 | 15,0 |
| 4:1 | 4,88 | 4,18 | 15,48 | 49,53 | 11,09 | 11,65 | 3,52 | 9,1 |
| 1:4 | 5,3 | 4,62 | 15,24 | 49,87 | 10,73 | 10,46 | 3,76 | 9,9 |
| CMC:CFLT | | | | | | | | |
| 1 % | 3,63 | 0,97 | 16,64 | 51,3 | 13,38 | 12,25 | 1,83 | 4,6 |
| 2% | 3,86 | 1,59 | 15,37 | 49,87 | 12,72 | 13,41 | 3,77 | 5,4 |
| 3% | 7,75 | 1,75 | 13,5 | 48,03 | 12,7 | 11,83 | 3,64 | 9,5 |
| CMC:DCG-GM | | | | | | | | |
| 1 % | 1,72 | 0,48 | 14,27 | 56,94 | 14,12 | 9,84 | 2,63 | 2,20 |
| 2% | 3,84 | 1,16 | 16,99 | 50,76 | 12,69 | 13,3 | 1,27 | 5,00 |
| 3% | 5,2 | 0,96 | 13,89 | 51,45 | 12,68 | 13,04 | 2,5 | 6,16 |
| CMC:PMAG | | | | | | | | |
| 1 % | 2,31 | 0,96 | 14,01 | 58,4 | 12,58 | 9,72 | 2,85 | 3,27 |
| 2% | 2,93 | 2,28 | 13,35 | 52,94 | 13,46 | 12,37 | 3,13 | 5,21 |



Table 4.17

**Influence of surface treatment of soil with IPC on dynamics of soil moisture* (%)**

| Experiment variant | 3rd day after seeding | | 10th day after seeding | |
|---|---|---|---|---|
| | Layer depth | | Layer depth | |
| | 0-5 cm | | 0-5 cm I 0-7,5 cm | |
| 2001 | | | | |
| Control | 8,9 h 8,7 | | 7,6 | 16,2 |
| CMC-UFR | 9,6 h 10,0 | | 8,8 | 18,1 |
| K-4- DCG-GM | 9,0 h 12,7 | | 9,5 | 17,0 |
| 2003 | | | | |
| Control | 9,4 | | 1,6 | - |
| CMC:PMAG | 14,3 | | 3,6 | |
| CMC-UFR+carbon-black | 13,6 | | 2,2 | - |
| CMC:CFLT | 12,1 | | 3,15 | - |
| CMC:DCG-GM | | | 2,12 | - |
| 2005 | | | | |
| CMC:PMAG | 13,1 | | 15,4 | - |
| Control | 8,7 | | 14,9 | - |

*Experimental data conducted in UzRCI in 2001, 2003, 2005.

Heat flows and soil temperature depend on its thermal conductivity, which in turn is due to the presence of a solid skeleton, the density of addition, the amount of moisture and water vapor.

Due to the high thermal conductivity of the water, the soil filled with it is more thermally conductive. The maximum thermal conductivity of the soil is observed in the upper layers in the spring during rains. The upper, less compacted soil layers, as they dry out, become less thermally conductive due to lower moisture and compactness. The less the compactness of the soil in the dry state, the lower the thermal conductivity of the soil layer, all other things being equal.

The thermal conductivity and the magnitude of the heat flux of the IPC are affected through the structure and moisture of the soil (Table 4.18). Measurement of soil temperature after application of IPC in an amount equivalent to a film of 15-20 microns thick to a highly compacted (up to 1.4-1.5 g/cm$^3$) upper centimeter layer of soil in laboratory conditions showed that the IPC alone in such a dose of strong influence evaporation

does not exert moisture and temperature distribution in the soil (Table 4.18). The soil temperature was measured at different moisture levels to determine when the treatment of the soil surface by the interpolymer complex is most effective.

Exceeding the temperature at a depth of 5 cm on wet IPC treated soils above the control was 1.8°C, on dry - only 0.6°C. Heat flows in this case lead to additional accumulation of heat in the spring period and warming the soil to May to a considerable depth. Due to the same effect, in the early morning hours the temperature under the IPC is higher and the night cooling is weaker. This is evident from a comparison of the results of the experiment and control (Table 4.18).

Table 4.18

**Data on soil temperature, °C (April 23-29 2005, UzRCI)**

| Experiment variant | Time of experiment, hour, min | 7,30 | | 14,30 | | 19,30 | |
|---|---|---|---|---|---|---|---|
| | Depth of measurement in soil, cm | 5 | 10 | 5 | 10 | 5 | 10 |
| | Soil temperature, °C | | | | | | |
| Control | | 19,51 | 19,1 | 29,9 | 27,7 | 28,0 | 26,6 |
| CMC-UFR | | 19,6 | 19,4 | 31,8 | 28,4 | 30,0 | 28,0 |
| K-4-DCG-GM | | 19,6 | 19,2 | 30,9 | 28,6 | 29,5 | 27,5 |

Additional warming of soil treated with IPC affects the temperature of the surface air layer. Systematic measurements of air temperature at an altitude of 10 cm from the soil showed that where the surface temperature of the soil is 2.0-2.5°C, the excess air temperature above the surface at a specified altitude is 0.2-0.3°C. These temperature extremes in soil and air in the plots processed by IPC are very important for optimizing the chemical and microbiological processes in the soil, as well as improving the physiology of the plants themselves in the spring, when there are productive moisture reserves in the soil and when, as a rule, the plant lacks heat.



## 4.10. IPC is a new mulch medium for cotton growing

The next necessary and especially important factor of the external environment, without which the growth and development of plants is impossible, is water. Normal development of seedlings and shoots of young cotton plants occurs when the moisture content of the root layer of soil fluctuates in the range of 70-100% of the maximum field moisture capacity. Both the excess and the lack of soil moistening negatively affects the vital activity of the cells of the bioorganism.

This level of soil moisture for cotton is optimal. It is achieved with the help of mulch means - soil conditioners optimizers.

In order to clarify the mulching properties of the IPC, we carried out small- and large-scale field experiments on cotton crops with deep mulching of the soil with interpolocomplexes and various known mulch devices such as sand, lignin, soil lumps with a diameter of -d = 2h5mm (soil mulch), mulch from soil lumps, treated with interpolymer complexes, and itself, IPC, applied over the soil mulch. Mulch was filled up to the depth of the seed laying, i.e. up to 4h5 cm. The width of the mulch material filling was different - from 2 to 4 cm, Table 4.19.

As the main indicator of the effectiveness of the action of the mulch medium, the cotton germination (%) and the capacity of its root system were adopted. But along with this, the humidity and temperature of the soil were measured at the experimental and control sites (Table 4.19.4.20). According to the data of the large-scale experiment (Table 4.20), mulching by soil clusters with a diameter of 2 to 5 mm treated with polycomplex gives a greater increase than in the case of IPC treatment of undivided soil. This is confirmed by the data of the study of small-scale experiments (Table 4.19).

It was revealed that the root system of cotton grows much more intensively with deep mulching. It is shown that the best mulch material can be made from the soil itself by treating it with polycomplexes.

Thus, the use of a new type of mulch means - IPC is an important reserve for increasing the productivity of cotton.

Research allows classifying IPC as an optimizer for the moisture and temperature regime of plant growth in serozem soils. IPC applied to the surface of the soil, weakens the intensity of evaporation from it during a prolonged drying out, which explains the increased soil moisture in the experimental area compared with the control one.

However, the IPC at the same time protects the soil from waterlogging during the rainy season. At the same time, the optimizing role of IPC during the re-moistening of the soil immediately after the rains is explained by another mechanism - the structure formation and changes in the volume of soil mass, which is processed by IPC. The volumetric weight of the arable layer of the soil changes markedly after the passage of the rains, namely, increases from 1.15-1.25 g/cm$^3$ to 1.3-1.6 g/cm$^3$, depending on the

Table 4.19

**Influence of interpolymer complex mulch resources on germination and cotton yield (small-plot experiments)**

| Mulch materials | Width of application mulch,cm | Thickness of mulch application,cm | Moisture of soil, % | | Soil temperature, °C | | Germination,% (after 25 mm of precipitation) | | Power of root systems | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | control | experiment | control | experiment | control | experiment | control | experiment |
| Sand | 2-4 | 5 | 18 | 16,5 | 25,5 | 26,6 | 91 | 33 | 62 | 20 |
| Lignin | 2-3 | 5 | 18 | 15,9 | 25,7 | 26,8 | 85 | 35 | 65 | 25 |
| Soil Mulch processed by IPC | 2-4 | 5 | 17,5 | 16,5 | 25 | 26 | 70 | 35 | 40 | 18 |
| PE film with thickness of 50 microns | 20 | 0 | 20 | 16 | 25 | 27,5 | 92 | 40 | 45 | 20 |
| Soil mulch + on top of IPC. 20 μm | 2-4 | 5 | 19 | 17 | 20 | 21 | 80 | 22 | 40 | 16,5 |
| Soil mulch | 2-4 | 5 | 19 | 18 | 25 | 25 | 50 | 40 | 28 | 18 |



duration and intensity of the rain. On the surface of soil treated with IPC, soil compaction occurs to a lesser extent, as evidenced by the fact that the bulk density varies from 1.15-1.25 g/cm$^3$ to 1.25 -1.4 g/cm$^3$ under the same conditions.

Thus, IPC can be used with great success in agriculture as a structure and mulch material. In this case, IPCs formed by the interaction between strong polyelectrolytes, can be used mainly as mulch material, and between weak polyelectrolytes - as structurants and mulch materials. As was said above (4.9), the use of IPC for surface treatment of soils leads to an improvement in its agrophysical properties.

It can be concluded that applying IPC to the soil provides an increase in seed germination irrespective of the weather conditions, improves the rate of plant development and, ultimately, increases the yield of cotton

Table 4.20

| Mulch materials | Average soil moisture for May,% | Soil temperature in May, ° C | Germination,% | Productivit, c / ha | Addition of harvest,c/ha |
|---|---|---|---|---|---|
| Control | 15,5 | 25 | 75 | 31 | - |
| Lignin + IPC | 18 | 26,5 | 90 | 42,4 | 11,4 |
| Soil Mulch processed by IPC | 17 | 26 | 90 | 36 | 5 |
| Undivided soil, processed with IPC | 17,5 | 26,2 | 85 | 34,4 | 3,4 |

### 4.11. The effect of polycomplexes on plant seedlings and soil microflora

In the previous sections, the effect of IPC on agrophysical properties of soils is considered. The results of the studies showed that the improvement of the structural state of soils under the influence of IPC leads to an increase in the yield of raw cotton. In this section, the direct effect of IPC as a chemical reagent on plant seedlings and on microorganisms of soils will be considered.

Studies of the effect of IPC on cotton seedlings were carried out in aqueous solutions of IPC of various concentrations for 35 days. The laboratory-miniature experiments with the germination of cotton in aqueous solutions of IPC of different concentrations show that polycomplexes do not inhibit plant seedlings. On the contrary, when

growing sprouts on the IPC CMC-PMAG solution, its stimulating effect on plants is observed. Table 4.20 provides observation data on the sixth day after sowing. It can be seen that IPC based on CMC-UFR and CMC-PMAG have a positive effect on the development of the root system of cotton. In plants, the seed germination increases in the CMC-PMAG solution, the growth of the main stem is outstripped, the stem root is much branched by the lateral roots, and the earlier appearance of these leaves is compared with the control. The best development of seedlings in experimental variants seems to be due to the presence of electrostatic interactions in the suspension under study and the presence of unbound low molecular weight PMAG fractions, which show a stimulating effect on cotton seedlings due to the presence of nitrogen in their chain.

Solution of the interpolymer complex CMC-UFR as CMC-PMAG has a positive effect on the development of the root system of cotton (Table 4.21).

Table 4.21

**Root system of cotton seedlings in solution with IPC (miniature experiments)**

| Indicators | Concentration of the solution, g/l | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0,0 | 0,005 | 0,01 | 0,05 | 0,10 | 0,15 | 0,20 | 0,50 |
| CMC-PMAG solution | | | | | | | | |
| Root stem length, cm | 22,5 | 15,0 | 16,2 | H.p. | H.p | H.p | - | - |
| Number of lateral roots of the 1st order, pcs. | 14,6 | 28,1 | 33,2 | 38,6 | 39,5 | 28,2 | - | - |
| Length of main stem, cm | 8,8 | 11,5 | 10,0 | 9,0 | 8,5 | 6,1 | | |
| Germination, % | 83 | 83 | 100 | 100 | 100 | 100 | - | - |
| CMC-UFR solution | | | | | | | | |
| Root stem length, cm | 10,0 | - | 11,9 | 8,7 | 8,6 | 10,3 | 9,8 | 4,1 |
| Number of lateral roots of the 1st order, pcs. | 10,2 | - | 19,1 | 11,1 | 16,9 | 20,1 | 22,4 | 7,3 |
| Germination, % | 66,6 | - | 90,0 | 73,3 | 76,7 | 86,3 | 80,6 | 56,6 |



It is known that the intensity of microbiological processes in the soil is affected by the content of organic matter, thermal, air and water regimes, the concentration of water-soluble salts and nutrients in the soil solution. We have shown the positive effect of IPC as a structurant and mulch medium on the indicated properties of soils.

Soils under cotton are inhabited by a huge number of microorganisms carrying out a great variety of biochemical processes. The development and activity of microorganisms in soil determines not only the formation and mineralization of soil humus, but also the inactivation of the products of the isolation of plants and the substances of inhibitory action that enter the soil under conditions of intensive chemicalization. The use of a variety of chemicals - herbicides, fungicides, defoliants, insecticides, etc., does not always have a positive effect on the development and activity of microorganisms, moreover, they destroy them.

For the widespread use in agriculture of polycomplex structurants it was necessary to determine their influence on the biological life of the soil.

An analysis of the literature data shows [299,300] that stabilization of lumpy soil structure under the influence of mulch means undoubtedly improves the conditions of vital activity of aerobic microorganisms.

It is also proved that the degree and specificity of the action of polymers on specific groups of microorganisms are different. Therefore, it was interesting to determine the effect of polycomplexes on the number of microorganisms in the IPC solution itself and the soil used in the laboratory experiment. The experiments were performed with a microorganism culture in Petri dishes with solutions of IPC CMC-UFR and CMC-PMAG. For this, the dose of IPC was taken in the following amount: CMC-UFR-0.0; 5,0 * 10-2 g / l; 7.5 * 10-2 g / l; CMC-PMAG - 5 * 1003 g / l; 2.510-2 g / l. After sowing the culture, holes were formed in the center of the Petri dish, and one drop of the IPC solution was poured into it.

Observations a week later showed that polycomplexes do not exert a depressing effect on this type of microorganism culture. At the same time, the development and life activity of microorganisms in the experimental variants did not differ from the control one.

The quantitative content of various physiological groups of microorganisms was studied by the method of deep sowing of limiting dilutions. The following groups of microorganisms were determined:

1. Amminifiers on the MPA medium.
2. Spore ammonifiers on meat-peptone agar + wort agar.
3. Microorganisms using mineral sources of nitrogen in the medium of KAA.
4. Oligonitrophylls on Ashby's medium.
5. Fungi on the environment of Czapek.

The results of the studies show that surface treatment of soil by various polycomplexes has a positive effect on the development of microorganisms. In the experimental variants, the total content of bacteria, actinomycetes, oligonitrophylls and fungi increases (Table 4.22).

Table 4.22

**The influence of various polymers on the development of soil microflora**

| Variant | Number of microorganisms, in thousands per 1 g of absolutely | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ammonifiers - meat-peptone agar (MPA) ( destroys the remains) | | | | Spore ammonifiers - meat-peptone agar + wort agar (MPA+WA) | | | |
| Observation days, days | 7 | 14 | 21 | 28 | 7 | 14 | 21 | 28 |
| Control | 8800 | 7200 | 4200 | 3100 | 53 | 47 | 32 | 25 |
| CMC+PMAG - 1 % | 4300 | 6100 | 5200 | 4900 | 66 | 52 | 35 | 27 |
| CMC+PMAG - 2 % | 2100 | 3150 | 4750 | 3500 | 55 | 49 | 39 | 29 |
| CMC+UFR - 1 % | 2900 | 3800 | 4300 | 3700 | 54 | 43 | 36 | 22 |
| CMC+UFR - 2 % | 2150 | 3200 | 2700 | 3300 | 102 | 98 | 73 | 53 |

Table continuation 4.22

| Microorganisms using mineral sources of nitrogen | | | | Oligonitrophilies Ashby Agar | | | | Mushrooms of Czapek | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7 | 14 | 21 | 28 | 7 | 14 | 21 | 28 | 7 | 14 | 21 | 28 |
| 6800 | 5100 | 4900 | 3700 | 6100 | 5300 | 4800 | 3400 | 18 | 12 | 8 | 6 |
| 23100 | 25500 | 13800 | 8700 | 11200 | 9200 | 6900 | 5500 | 14 | 10 | 6 | 3 |
| 25000 | 28500 | 19500 | 13500 | 13500 | 10800 | 9500 | 6700 | 18 | 16 | 9 | 4 |
| 12900 | 19000 | 14500 | 11500 | 10200 | 8500 | 5800 | 4700 | 12 | 10 | 7 | 3 |
| 15500 | 16700 | 15100 | 12300 | 12800 | 9700 | 6100 | 5200 | 18 | 16 | 8 | 4 |

As described above, polycomplexes based on a polymer of natural origin and sodium carboxymethylcellulose amine oligomers and polymers (UFR, PMAG) is easily degraded and the final product of degradation in soil can serve as nutrition for the plants. Studies on the study of the vital activity of microorganisms in soil treated with polycomplex confirm this position. As is known, ammonifiers are organisms that actively destroy



various organic remains before their full mineralization. Table 4.22 shows that on the 7-10th day after the beginning of the experiment, the number of ammonifying bacteria in all experimental variants was 4-6 thousand lower than in the control variant. Further increase in the number of these groups of bacteria is observed up to the level in the control. On the 28th day of observations in the control variant of the experiment, the number of bacteria decreased, and in variants containing IPC, their numbers become higher than in the control experiment. At 1 thousand 800 on the option CMC-PMAG (1% solution) and CMC-UFR (1% solution). This, apparently, is due to the fact that the destruction of polycomplexes begins with time, and the destruction products increase the growth and life activity of ammonifying bacteria. Such a process is of no small importance for the life of the soil. Studies with other groups of microorganisms also show that IPC promotes the development of microorganisms. For example, the total number of microorganisms using mineral sources of nitrogen was 6800 thousand tons/g, and in the experimental version - 23100 thousand/g, i.e. in 3 times more. Accordingly, the content and oligonitrophylls increase.

At the same time, there was no clear dependence of the influence of polymers on the change in the quantitative composition of spore bacteria. However, by 28 days there has been a decrease in the number of all detectable groups of microorganisms in all variants of the experiment, but still the number of bacteria in the variant with IPC remains higher than in the control one.

Observations carried out on the growth and development of cotton in these experiments show that improved soil conditions favorably affected the life of plants. In all terms of observation, cotton growth in variants with IPC was higher, the area of the cotyledonous leaves was larger than the control ones.

## CONCLUSION

Interest in the study of intermolecular reactions is due to the fact that the products of these reactions - polymer complexes, in particular polyelectrolyte (PEC) and polycomplex (PC), reveal a number of valuable properties and are already used in some branches of technology, water, agriculture and medicine. They are essentially polymeric materials with a complex of new properties, although they were obtained in most cases from known polymers by simply mixing solutions of interacting polymer components in a common solvent. This opens up new ways of rational use of known traditional polymers.

Reactions between macromolecular components include such a promising area of polymer chemistry as matrix synthesis, which gives ample opportunities for the production of polymers of a certain structure.

In recent years, interest has increased in the binding of medicinal substances by organic polymers, in particular, polyelectrolytes, which leads to the prolongation of the action of the drug in the body. The process of complexation of drugs with polymers is associated with the appearance of intermolecular forces and the formation of supramolecular structures that easily change under the influence of external factors.

In connection with the expansion of the field of practical application of interpolymer complexes (IPC), the problem of protecting the environment and saving water resources becomes especially topical.

This monograph is devoted to the study of the possibility of formation and properties of interpolymer complexes stabilized by ionic and H-bonds in carboxymethylcellulose and amine-containing polymer systems.

*The authors conducted the following studies and presented their own results:*

1. The main principles of creating interpolymer composite materials based on carboxymethyl cellulose, aminosulfide compounds and dispersed fillers are formulated. The role and characteristics of complementary macromolecules in the formation of inter-polymer complexes and composite materials with special properties are revealed.

2. The specific features of the interaction of carboxymethylcellulose (CMC) with urea-formaldehyde resins (UFR), polyhexamethyleneguanidine (PGMG), polymethylene aminoguanidine (PMAG) and natural-serine sericin (NSS) have been studied. It was found that at a certain pH value and the ratio of the constituent components due to ionic and hydrogen bonds, it is possible to obtain interpolymer complexes (IPCs) of both stoichiometric and non-stoichiometric compositions. It was shown that for non-stoichiometric complexes the microheterogeneous structure is very characteristic, which causes low values of the modulus of elasticity and other physicochemical parameters of the samples.

3. From the point of view of medico-biological properties of interpolymer complexes, it is shown that interpolymer complexes are



thrombosed with blood contact, i.e. interpolymer complexes are thrombotic-resistant materials.

4. Binding of heparin antagonist to the polymer complex leads to a decrease in toxicity and does not change the anti-heparin activity of the drug. The release of heparin antagonist occurs in strictly therapeutic doses, and the excess antagonist is not present in a free form, but in the composition of a low-toxic soluble non-stoichiometric interpolymer complex.

5. The synthesized IPEC based on eudragit marks E100 and L100 as a new polymer carrier will allow expanding the range of polymers produced by RxhmPharma Company, used in the development of oral dosage forms with controlled release.

6. The composition of the formulation containing a salt of polyhexamethylene guanidine and protease "C" (such as an antimicrobial substance, its molecular weight and the ratio of components) was found to influence the activity, stability, and pH-profile of the enzyme activity. It is shown that in the preparation of compositions with combined biological activity the greatest stabilizing effect on the immobilized protease "C" is provided by PGMG-X with a MM of 15 kDa. A change in the pH profile of the action of the immobilized protease "C" was established, which is a consequence of the destruction of the initial enzyme complex as a result of complexation with PGMG.

7. The structural and mechanical properties of concentrated aqueous solutions of Na-CMC and its complexes with UFOs in various ratios of components have been studied. It is shown that aqueous solutions of Na-CMC are thixotropic systems. The introduction of urea-formaldehyde oligomers into Na-CMC solutions leads to the degeneration of the thixotropic effect. At high shear stresses, intermolecular associates are destroyed, with simultaneous destruction of the polycomplex and polycomplex gel.

8. A calculation method for evaluating the effectiveness of the influence of the inter-polymer complex on the basic erosion properties of the soil is proposed. It is shown that the anti-erosion and anti-deflation effects of the interpolymer complex depend both on the properties of the soils and on the characteristics of the complex. It has been experimentally proven that the effect of anti-erosion and anti-deflation actions recommended.

9. Field tests have ascertained that the developed interpolymer complexes and composites with an excess of carboxymethyl cellulose can be used as highly swelling hydrogels and an anti-filtration screen, and with an excess of urea-formaldehyde resin and dispersed fillers to save irrigation water (due to uniform distribution water along the length of the irrigation sulcus). An increase in cotton yields of 4-6.3 centner / ha was noted.

10. Scientific bases for the application of environmentally friendly, economically accessible interpolymer complexes based on carboxymethyl cellulose and amine-containing urea-formaldehyde resins and polymers have been developed to improve the agrophysical properties of soils. Approaches to the creation of polycomplexes with given properties for solving specific problems in agriculture, including for preventing soil caking, are demonstrated.

11. Formulations based on interpolymer complexes have been developed and introduced in agriculture as structurants and mulch materials used to create favorable agrophysical conditions for the growth and development of plants, as well as for reclamation, for the creation of anti-filtration screens and as moisture distributors in the soil in order to reduce depth filtration and saving of water resources in arid zones of the republic.

12. Successful field trials on the use of the developed interpolymer complexes as binding dispersion systems for efficient dust suppression and radionuclide localization on the surface of the alienation ground of the Chernobyl nuclear power plant, as well as to prevent salt and dust transfer in the open areas of the bottom of the Aral Sea were conducted. Optimum compositions of formulas and norms of their consumption have been ascertained.



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The monograph gives a comparative evaluation of using interpolymer complexes in medicine, water economy and agriculture. Methods of preparation, physicochemical, mechanical properties and their structures are shown and the possibility of using interpolymer complexes as new materials for the formation of artificial blood vessels, biocompatible materials; thrombus resistance, as well as the relationship between the waterproof macrostructure and the functional properties that determine the productive capacity, corticity, soil erodibility; saving irrigation water. An original and promising way of using interpolymer complexes in medicine, water and agriculture for the rational use of water resources and protection of soils and the environment is proposed. It can be used for chemists, physicists, pharmacists, physicians, soil scientists, meliorators, graduate students, researchers and students of higher educational institutions.

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