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INTERACTION OF LINEAR POLYELECTROLYTES WITH OPPOSITELY CHARGED LIGHTLY CROSS-LINKED NETWORKS

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Abstract: The processes proceeding at the contact of highly swollen lightly cross-linked polyelectrolyte networks with aqueous solutions of oppositely charged linear polyions were studied. The reactions under discussion proceed as frontal processes and follow by strong (three orders of magnitude) contraction of the gel sample. The existence of sharp boundary between outer weakly swollen layer which is the reaction product—interpolyelectrolyte complex and the highly swollen inner part which is the initial unconverted gel is characteristic for the process. The kinetics of linear polyions absorption by polyelectrolyte networks and factors controlling the rate of sorption such as chemical structure of polyelectrolytes, nature and concentration of simple salts, pH, temperature were investigated. The "relay-race" mechanism of linear polyelectrolyte transport was established.

INTRODUCTION

It is well known that oppositely charged linear polyelectrolytes interact one with another strongly and cooperatively to form the stable interpolyelectrolyte complexes (Refs. 1-3). Recently it was found that linear polyelectrolytes are able to interact cooperatively also with oppositely charged water swollen polyelectrolyte networks (Refs. 4-7). In some cases this interaction is constrained by the absorption of linear polyions on the hydrogel surface and by the formation of very thin surface layer of interpolyelectrolyte complex (IPEC). In other cases linear polyions are able to penetrate into the polyelectrolyte gel and give rise to collapse

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of latter. In some or other way the properties of the gel surface is strongly changed. The polyelectrolytes of different nature such as synthetic and also natural in particular proteins, polysaccarides, DNA can be used as hydrogels modifiers. The IPECs formed as a result of the interactions between oppositely charged networks and linear polyelectrolytes are much less studied in comparison with those formed by linear polyelectrolytes. In this paper the peculiarities of the interpolyelectrolyte reactions (IPR) between oppositely charged lightly cross-linked and linear polyelectrolytes and also the structure of IPECs formed are discussed.

EXPERIMENTAL PART

We have studied the interaction of aqueous solutions of polycations such as poly(N-ethyl-4-vinylpyridinium bromide) (PEVP) of weight-average polymerization degree P_w = 300, 350, 1500, 1600 and 2700, polyethylenemine hydrochloride (PEI·HCl), P_w=1400, and poly(N,N-dimethylaminoethyl methacrylate hydrochloride) (PDMAEM·HCl), P_w = 400, with poly(sodium acrylate) (NaPA) gel. Interaction of aqueous solutions of linear polyanions such as NaPA, P_w = 200 and 500, poly(sodium styrenesulfonate) (NaPSS), P_w = 22 and 500, poly(potassium vinylsulfate) (KPVS), P_w = 700, and heparin, a natural polysaccharide containing sulfate groups, with PDMAEM·HCl gel were studied as well.

The polyelectrolyte gels were obtained by means of radical polymerization of corresponding monomers in the presence of 1 wt.-% of the cross-linking agent N,N-methylenebisacrylamide. Concentration of repeating units in equilibrium swollen PANa and PDMAEM·HCl ionized gels was about 10^{-2} base mol/l. The concentration of the linear PEVP and NaPSS in aqueous solution was measured spectrophotometrically by the absorption band intensity at λ=257 and λ=225 nm, respectively. The concentration of poly(acrylic acid) (PAA) and PDMAEM in the solution were measured by means of potentiometric titration. Spectrophotometric measurements and potentiometric titration were carried out on the "Hitachi" 150-20 spectrophotometer (Japan) and the "RT 822" autotitrator (Denmark), respectively.

RESULTS AND DISCUSSION

Absorption of linear polyelectrolytes by oppositely charged lightly cross-linked polyelectrolytes.

When the piece of charged, equilibrium-swollen in water, polyelectrolyte gel is immersed into aqueous solution of oppositely charged linear polyelectrolyte, the concentration of the latter is decreased. This means that gel absorbs the linear polymer. The capacity of the gel to linear polyelectrolyte providing them both are fully charged is determined by the condition of electroneutrality of IPEC formed. In terms of interaction between cross-linked and linear polyelectrolytes it means that IPR proceeds up to completion i.e. all of the monomer units of the network are able to form the salt linkages with the monomer units of linear polyelectrolyte. In the other words the network is fully penetrable for the linear polymer.

It is clear that this process takes certain time which depends on the chemical nature of the reacting polyelectrolytes and on the external conditions such as the nature and the concentration of salt, pH, temperature etc. The typical kinetic curve of absorption of linear polyions by the oppositely charged network is shown in Fig.1.

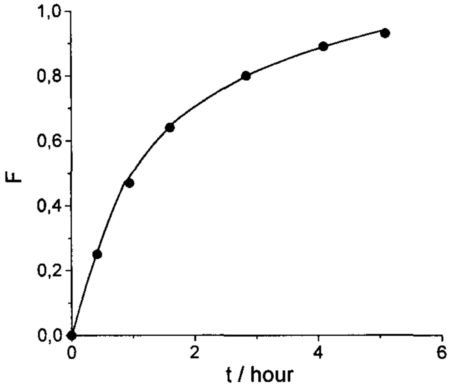
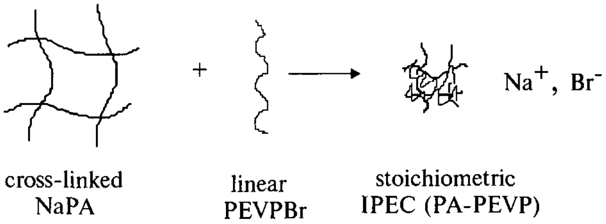


Fig.1. Absorption kinetics of PEVP, Pw=350, by NaPA gel from salt-free aqueous solution; the sample of the initial gel was prepared in the form of cube with mass about 1g. [PEVP]=10^{-3} base mol/l; T=25°C.

This Fig.1 corresponds to the absorption of PEVP fraction with the degree of polymerization P_w =350 by the lightly cross-linked sodium polyacrylate (NaPA) from salt-free aqueous solution. It is seen that the process is completed with the full conversion of network into the IPEC at F=1, where F is the degree of completion of the absorption process. In this case absorption is completed in five hours with the formation of the stoichiometric IPEC, PA-PEVP, which contains the equivalent amount of PA carboxylate and PEVP pyridinium groups and the network is not able to absorb the excess amount of linear polyions if they are present in the solution. This means that the IPR between cross-linked and linear polyelectrolytes shown below spreads over the intire gel volume.



(1)

It is worthy of note that the IPR proceeds up to complete depletion of the linear polyions in the case the latter are present in deficiency relatively to the cross-linked polyelectrolyte. It means that the equilibrium concentration of linear polyions in the surroundings is equal zero and the isotherm of binding of linear polyions by the oppositely charged network is pressed to the ordinate axis and practically coincides with it.

The capacity of gel to linear polyelectrolyte is strongly dependent on the degree of dissociation, α, both linear and cross-linked polyelectrolytes and it is the higher the lower the degree of dissociation of linear polyelectrolytes. In terms of the IPR (1) it means that the composition of IPEC formed changes with changing of the degree of dissociation both polyelectrolytes. The compositions of IPECs, $\varphi=[\ell PE]/[crPE]$, where $[\ell PE]$ is the concentration of linear polyelectrolyte monomer units and [crPE] is the concentration of cross-linked polyelectrolyte monomer units incorporated into IPEC, are listed in the Table 1 for various systems at different pH and correspondingly at different values of α.

Table 1. Composition of IPECs formed by the oppositely charged cross-linked and linear polyelectrolytes.

System	Dissociation degree of polybase	Dissociation degree of polyacid	φ=[Polybase]/ [Polyacid]
Cross-linked PAA - linear PDMAEMA	1	0	0.3
	1	1	1
	0	1	2.5
	0.45	1	1.5
	0.75	1	1
Cross-linked PAA - linear PEI	1	0.05	0.6
	0.1	1	2.8
	0.3	1	2.0
	0.6	1	1.0
Cross-linked PAA - linear PEVP	1	0.2	0.5
	1	1	1
Cross-linked PDMAEMA - linear PAA	1	0	0.3
	1	0.3	0.7
	1	0.6	1
	1	1	1
	0.1	1	2.5
	0.25	1	2.2
	0.40	1	1.5
	0.55	1	1
	0.70	1	1

It is seen that the products of complete IPR (1) which are formed at low charge (low α) of the cross-linked polyelectrolyte are depleted of linear polymer in comparison with the stoichiometric IPECs. This corresponds to lower capacity of gel. In contrast, IPECs formed in the conditions of low charge (low α) of linear polyelectrolyte are enriched in it and correspondingly the network exhibits high capacity to linear polyelectrolyte. These observations are in good agreement with data on the effect of the degree of dissociation polyelectrolytes on the composition of IPECs formed by oppositely charged linear polyelectrolytes (Refs. 8,9).

It is important that in strongly acid or strongly alkali media in which one (or both) of reacting polyelectrolyte is discharged, so the equilibrium of IPR (1) is completely shifted to the left, one cannot find any absorption of linear polyelectrolyte by the network. Moreover if the IPEC formed by cross-linked NaPA and linear PDMAEMA·HCl is immersed into alkali aqueous solution at pH>11 one can see that PDMAEMA is released from IPEC gel into the surrounding solution. In due time (ca. 3 hours) practically all that weak polybase included initially in IPEC is detected in the surrounding alkali solution. It means that the driving force of absorption of linear polyelectrolytes is the gain of free energy as a result of IPR (1) accompanied by IPEC formation. Thus when we study the absorption of linear polyions by the oppositely charged polyelectrolyte gels we deal with the activated diffusion phenomena.

Collapse of the polyelectrolyte networks as a result of the interaction with oppositely charged linear polyions.

When one put the sample of lightly cross-linked polyelectrolyte gel into the aqueous solution of oppositely charged linear polyelectrolyte the strong diminution of the sample volume (weight) together with the absorption of linear polymer is observed. The weight of the initial equilibrium swollen gel samples (m_o) and that of corresponding IPECs (m_i) are shown in Table 2. In this Table the ratios m_o/m_i for different systems are shown also.

It is seen that polyelectrolyte gels subject to very strong collapse as a result of the interaction with oppositely charged linear polyions. This is reflected by the values of m_o/m_i which run into 100 or even more. Obviously the release of small osmotically active network counterions into surroundings by the IPR (1) is responsible primarily for the gel collapse. The swellability, $H=(m_w-m_d)/m_d$ (where m_w - is the weight of the swollen IPEC and m_d - is that of the dry IPEC sample) of IPECs formed as a result of IPR (1) is rather low and add up to H=1 ordinarily.

Table 2. The weight of the initial equilibrium swollen NaPA gel (crNaPA) samples (m_o), that of corresponding IPECs (m_i) and the ratios m_o/m_i.

System	m_o, g	m_i, g	m_o/m_i
crNaPA	1.0		
crNaPA-PDDAACl		0.004	250
crNaPA-PEI·HCl		0.006	170
crNaPA-PDMAEMA·HCl		0.004	250

It is very important to note that the collapse of gel induced by IPR (1) is the continual process in contrast with the known classical abrupt gel collapse induced by the changes in the composition or temperature of the surroundings (Refs.10-12). It is seen in Fig 2. in which the dependence of the ratio m_o/m_i for NaPA gel on the degree of absorption F of PDDAACl, PEI·HCl and PDMAEMA·HCl are presented.

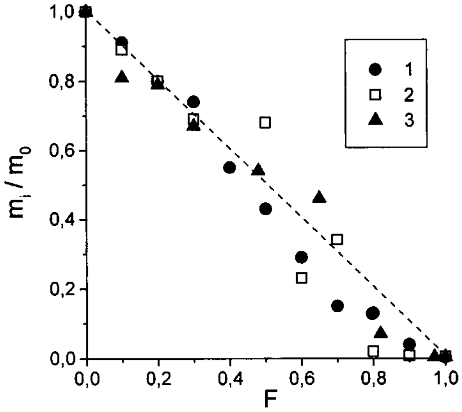
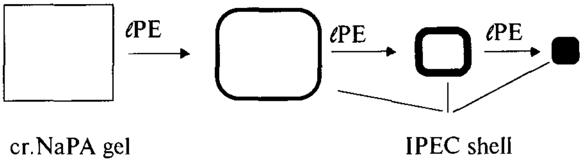


Fig.2. The dependence of the ratio $\mathbf{m_o/m_i}$ for NaPa gel on the degree of absorption (F) of PDDAACl (1), PEI·HCl (2) and PDMAEMA·HCl (3) from salt-free aqueous solutions; the samples of initial equilibrium swollen gel were prepared in the form of cubes with mass about 1g; the concentration of linear polyelectrolyte in solution was 10^{-3} mol/l.

Fig.2 shows that the weight of the gel sample decreases practically linearly (with negative deviations in the region of high F values which are beyond the scope of this paper) with the increase of amount of absorbed linear polyelectrolyte, i.e. as IPR(1) runs. It means that in the case of the interaction between oppositely charged cross-linked and linear polyelectrolytes we deal with the new phenomenon of localized gel-collapse. Only that part of the gel sample which is converted into IPEC collapses. At the same time nonconverted part displays the same swellability as the initial gel. One can easy observe the localized collapse by his own eyes in a very simple experiment. Shortly after immersing the polyelectrolyte gel sample into the solution of oppositely charged linear polyelectrolyte the very thin rainbow film appears on the sample surface. The surface film becomes thicker and opaque in due time. This process is shown in the scheme (I).



(I)

There is a sharp boundary between this IPEC surface layer and gel interior. This sharp IPEC-gel interface moves inside the initially transparent gel as the IPR(1) goes on, so that the IPEC layer gradually thickens. The process may be interrupted at any stage through taking the gel sample out of the solution of linear polyelectrolyte. After this the outer relatively strong IPEC layer can be separated mechanically from the interior nonconverted highly swollen gel. The compositions of these separated parts of the test samples composed of different cross-linked and linear polyelectrolytes were analyzed via elementary analyses. The data of analyses are presented in Table 3.

It is seen that the whole linear polymer absorbed by the gel was detected in the outer layer as a component of IPEC and no linear polymer was detected in the interior unconverted gel. It is worthy of note that the composition of outer IPEC layer in the products of incomplete IPR(1) which are presented in Table 3 coincides with that of products of complete IPR(1) which are shown in Table 2.

Thus the process of interaction between cross-linked and oppositely charged linear polyelectrolytes can be represented as continuous conversion of highly swollen initial gel phase which is in the interior of the sample into newly formed compact IPEC phase which is in the outer layer of the sample proceeding in the macroscopically heterogeneous system.

Table 3. The composition of the separated shell and core parts of the gel samples - the products of incomplete IPR.

System	Dissociation degree of polybase	Dissociation degree of polyacid	φ=[Polybase]/ [Polyacid] in the interior (core)	φ=[Polybase]/ [Polyacid] in the outer layer (shell)
Cross-linked PDMAEMA - linear PAA	1.0	0	no linear polymer was detected	0.3
	0.1	1.0		2.5
Cross-linked PAA - linear PDMAEMA	1.0	0.1		0.25
	1.0	1.0		1.0
Cross-linked PAA - linear PEVP	1.0	0.2		0.5
	1.0	1.0		1.0

It is important to note that the macroscopically two-phase systems of "core-shell" type are thermodynamically stable. This conclusion is followed from the behaviour of products of incomplete reactions. When we put the two-phase sample into pure water we cannot reveal any changes in it for a long time (more than month and much more than it is necessary to convert whole gel sample into IPEC, see Fig.1). The sample conserves its weight and the sharp boundary does not move and diffuse. It is not surprising as far as the entropy loss due to the network contraction is minimal for the macroscopically two-phase system.

The mechanism of linear polyelectrolyte transport into oppositely charged gels.

The driving force of the active transport of linear polyions into oppositely charged networks, as shown above, is the free energy of interpolyelectrolyte addition reaction (1) which is accompanied by the IPEC formation. This reaction proceeds on the solution — IPEC interface and as a result the IPEC outer shell is formed, which is separated from the gel interior with sharp boundary. The IPEC shell moves from outside to the gel sample interior in the course of the IPR (1). It is illustrated by the scheme (I).

The rate of moving of the inner boundary between gel core and IPEC shell is strongly dependent on the degree of polymerization of linear polymer, P_W. The data on the kinetics of absorption of different PEVP fractions by equilibrium swollen NaPA gel from neutral aqueous solution are presented in Fig.3.

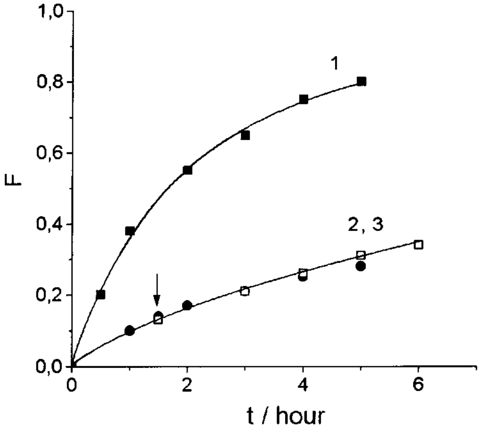
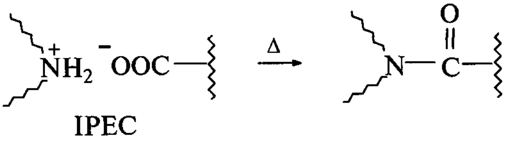


Fig.3. Absorption kinetics of PEVP of different polymerization degree by NaPA gel from salt-free aqueous solution: P_W=300 (1); P_W=1500 (2); P_W=300, but the initial gel was brought into contact with PEVP, P_W=1500, solution before the beginning of the measurement (3). [PEVP]=$6 \cdot 10^{-3}$ base mol/l; the samples of the initial gel were prepared in form of cubes with mass about 3 g; T=25°C.

From the comparison of curves (1) and (2) it follows that the absorption rate decreases considerably with the increase of P_W. This quite expectable and obvious result was used to realize the character and peculiarities of transfer of linear polyions through the outer shell. In order to do that, the gel sample was initially placed into a high molecular PEVP (P_W =1500) solution for some time (ca. 1.5 h) (this point is marked by the arrow on the curve 2), so that the thin IPEC layer containing relatively long polycations was obtained on the gel surface. Then this sample was transferred into the relatively low-molecular PEVP (P_W=300) solution, and the absorption kinetics of short polycations was measured (Ref.6). The latter kinetic curve 3 coincides with the curve 2 corresponding to absorption of high-molecular PEVP (P_w=1500) as seen from Fig.3. The obtained results bring in evidence the "relay-race" mechanism of transfer of linear polyions in the gel network. The "relay-race" mechanism was verified also via another experiments (Ref.6). It was found that the absorption of linear polyions by the oppositely charged polyelectrolyte gel can be suppressed by the creation of chemical cross-links between oppositely charged chain segments incorporated in the IPEC shell. It can be easily done for the IPEC formed by PEI and cross-linked NaPA. The interchain salt bonds in this IPEC are converted to amide bonds at elevated temperature as shown below:



(2)

The degree of conversion in the reaction (2) was shown in the case of IPEC formed by the pair of the same but linear polyelectrolytes is easily controlled by the reaction temperature (Refs.13,14).

The thin surface layer of IPEC was prepared by immersing of NaPA gel sample into the solution of PEI·HCl for ca. 30 min. Then the sample was placed into an ampoule filled with water and heated in autoclave at 150° C for 1 h. These conditions lead to formation of 3-5 amide bound per 100 salt bonds in IPEC. The kinetics of PEI·HCl absorption by two similar NaPA gel samples, one of which had the thin chemically cross-linked IPEC surface layer, is shown in Fig.4.

The point of intersection of the curves 1 and 2 corresponds to the time of interruption of the absorption process for the sample 2, that subjected just after to the thermal treatment. It is seen that this sample 2 lost the ability to absorb PEI·HCl. This observation demonstrated impermiability of IPEC immobilized layer for the linear polyions and proves the "relay-race" mechanism of their absorption

This mechanism of absorption assumes that the transport of linear polyions into the gel proceeds as a frontal heterogeneous interpolyelectrolyte reaction without the radial mixing of penetrated polyions. The latter claim was also experimentally proved via the study of absorption of the mixture of two PEVP narrow fractions with $M_w=1.5\cdot10^5$ and $M_w=0.5\cdot10^5$ by NaPA gel (Ref.15).

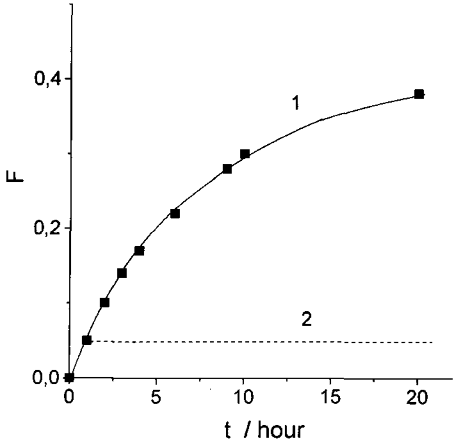
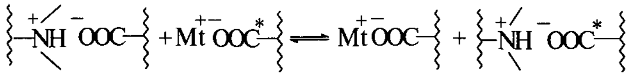


Fig.4. Absorption kinetics of PEI•HCl, P_w=200, by NaPA gel from salt-free aqueous solution; the sample of the initial gel was prepared in the form of cube with mass about 10g. $[PEI \cdot HCl]=5.10^{-3}$ base mol/l (1); absorption kinetics curve for the thermally treated partially converted sample (2); T=25°C.

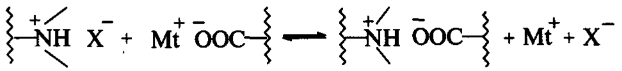
The lack of fractionation in the result of absorption revealed in our experiments confirms also the "relay-race" mechanism of the process under study. It means moreover that there is no linear polyion exchange between IPEC and external solution, i.e. the linear polyion bounded with the segments on the network surface moves into the gel interior rather quickly. So polyions can leave the gel-solution boundary for the time which is not sufficient to set in the thermodynamic equilibrium between gel and solution.

Thus it follows from the data presented above that the directed active transport of linear polyelectrolytes in oppositely charged gels represents a "relay-race" transfer of linear polyion segments from one fragment of the polyelectrolyte network to the other via interpolyelectrolyte exchange reaction (IPER). The cooperative IPER may be represented by the following set of the elementary reactions:



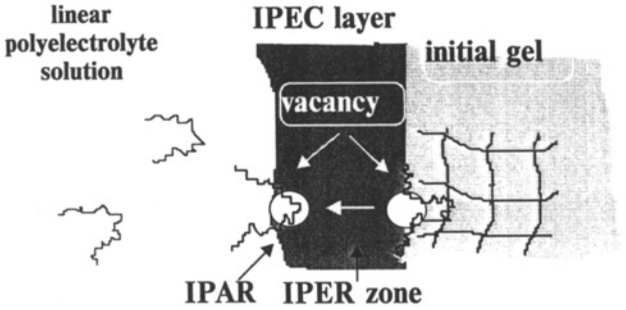
$$\sim\overset{+}{N}H\ \overset{-}{O}OC\sim + \overset{+}{Mt}\ \overset{-}{O}OC^{*}\sim \rightleftharpoons \overset{+}{Mt}\ \overset{-}{O}OC\sim + \sim\overset{+}{N}H\ \overset{-}{O}OC^{*}\sim \qquad (3)$$

The IPER produces "vacancies" in the IPEC layer, which are charged segments of the network surrounded by an equivalent quantity of low-molecular counterions. The vacancies migrate in the same way (via the IPER (3) repeated many times) through the IPEC layer to the IPEC — solution interface, where they react immediately via the interpolyelectrolyte addition reaction (IPAR) with free linear polyions supplied from the solution. The IPAR (4) presents a set of elementary reactions between monomeric units of the interacting chains:



$$\sim\overset{+}{N}H\ \overset{-}{X} + \overset{+}{Mt}\ \overset{-}{O}OC\sim \longrightarrow \sim\overset{+}{N}H\ \overset{-}{O}OC\sim + \overset{+}{Mt} + \overset{-}{X} \qquad (4)$$

At the same time, the low-molecular electrolyte is released in the solution. This is illustrated by the scheme (II).



(II)

The kinetics of linear polyelectrolytes absorption by oppositely charged lightly cross-linked polyelectrolytes.

A typical kinetic curve corresponding to the absorption of linear PEVP cations by the lightly cross-linked NaPA is shown in Fig.5. Points 1 and 2 correspond to the absorption of linear polycations from PEVP solutions having different concentrations. It is seen that in the range of PEVP concentration 10^{-4} -10^{-3} base mol/l the rate of polycation absorption by the gel is independent of the linear polyelectrolyte concentration in the surrounding solution. The absorption rate also does not depend on the solution stirring speed. So the process of absorption has the inner diffusion character. Nevertheless the kinetics of sorption in the case under consideration cannot be described within the framework of the usual diffusion models. The curves of the absorption kinetics are not linearized in the F versus $t^{1/2}$ coordinates even in the initial step.

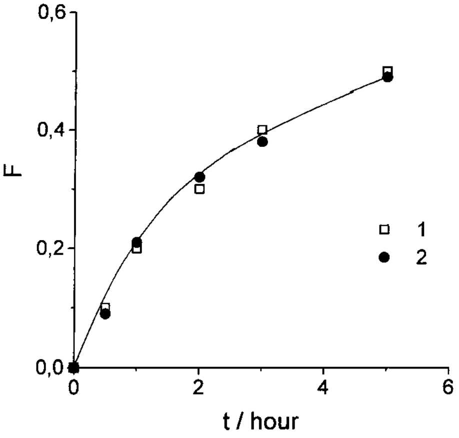


Fig.5. Absorption kinetics of PEVP, P_w=1600, by NaPA gel from salt-free aqueous solution; the samples of the initial gel were prepared in the form of cubes with mass about 1g. [PEVP]=10^{-3} base mol/l (1), 10^{-4} base mol/l (2); T=25°C.

As it was shown above the penetration of the linear polyions inside the gel proceeds via the IPER (3) between the IPEC formed as a result of IPAR (4) and the free network fragments (see scheme (II)). The IPAR (4) occurring on the outer surface of the gel sample cannot be a factor determining the overall rate of sorption because it is known that this reaction is almost instantaneous (Ref.16). Therefore, the rate of transfer of linear polyions from the surrounding solution to the gel volume is controlled by the IPER (3) in the IPEC layer. Thus, as one should expect, the factors affecting the IPER (3) rate will determine the kinetics of linear polyelectrolyte absorption by the oppositely charged gel.

It is well known that the rate of IPER proceeding in the systems composed of oppositely charged linear polyelectrolytes is strongly dependent on the chemical structure of polyelectrolytes in particular on their linear charge density, on the nature and concentration of low molecular electrolytes, on pH etc. (Ref.16). We have studied the effect of the simple salt concentration on the rate of linear PEVP absorption by the cross-linked NaPA. The kinetic curves of PEVP absorption from the aqueous solutions containing different concentrations of NaCl are shown in Fig.6.

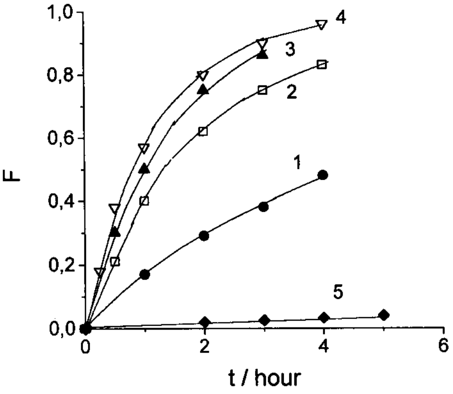


Fig.6. Kinetic curves for sorption of linear PEVP (P_w=1600) by NaPA gel from aqueous-salt solutions of various ionic strengths; [NaCl] (mol/l) = 0 (1); 0.02 (2); 0.1 (3); 0.5 (4); 1.0 (5); the samples of the equilibrium swollen in corresponding aqueous-salt solutions NaPA gel were prepared in the form of cubes with mass about 1g. [PEVP]=10^{-3} base mol/l ; T=25°C.

From the comparison of the curves 1, 2, 3 and 4 it is seen that the increase in NaCl concentration to 0.1 mol/l produces a significant increase in the rate of absorption of PEVP. These observations are in qualitative agreement with our findings on the effect of simple salts on the IPER kinetics in the systems composed of oppositely charged linear polyelectrolytes. This effect is caused by the fact that weakening of electrostatic interaction between oppositely charged linear and cross-linked polyelectrolytes markedly facilitates the transfer of linear polyions from one network segment to another. When the NaCl concentration exceeds 1 mol/l the rate of absorption sharply drops, see curve 5 in Fig.6. For such a high salt concentration the electrostatic interaction between linear and cross-linked polyions is screened by counterions and virtually vanished. It means that IPAR (4) almost ceases under these conditions and, hence, the source of free energy that is necessary in order to provide the active transport of linear polyions to the gel disappears.

As it was demonstrated above in Fig.3 the rate of transfer of the linear polyions in an oppositely charged gel depends on the chain length of penetrating macromolecule. An increase in the degree of polymerization markedly decreases the rate of linear polyion sorption by the polyelectrolyte network.

The rate of transfer of linear polyions in a gel markedly increases with temperature. The activation energies calculated from the initial portions of the kinetic curves of absorption of various PEVP fractions (P_w= 350, 700,1600, and 2700) by the NaPA gel are close to one another and amount to approximately 40 kJ/base mol (Ref.17). This reflects the segmental character of motion of the linear polyions in the gel phase.

The size of the kinetic unit participating in the transfer event apparently depends on the chain rigidity and conformation. In Fig.7 the kinetic curves for absorption of positively charged rigid-chain polysaccharide, chitosan, by NaPA gel (curve 1) and that of rigid-chain polyanion of sodium carboxymethylcellulose (NaCMC) by PDMAEM·HCl gel (curve 3) are shown in comparison with the kinetics of penetration of flexible-chain polyelectrolytes having the same degree of polymerization.

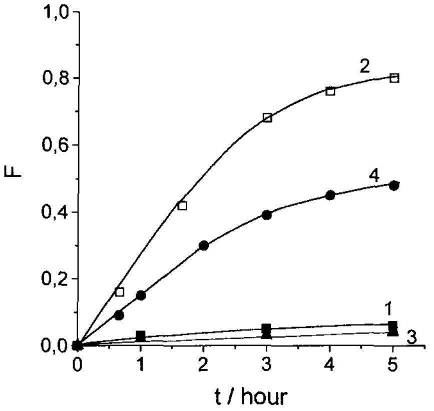
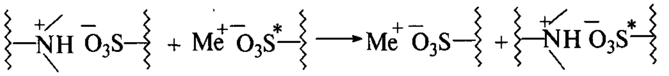


Fig.7. Kinetic curves for the absorption of chitosan (P_n=700) (1) and PEVP (P_w=700) (2) by NaPA gel; and of NaCMC (P_n=500) (3) and NaPA (P_w=520) (4) by PDMAEM·HCl gel; the samples of equilibrium swollen gels were prepared in the form of cubes with mass about 1g; [NaCl]=0.02 mol/l; T=25°C

From the comparison of curves 1 and 2 and also 3 and 4 in Fig.7 it can be seen that the absorption of the flexible-chain linear PEVP and NaPA proceeds at a much greater rate.

The kinetics of linear polyelectrolyte transport into the gel is strongly dependent on the chemical structure of former. As it was shown above the polyanions with carboxylic groups are able to penetrate the positively charged gels more or less rapidly. The contrary is the case when linear polysulfate and polysulfonate anions with high linear charge density are as the penetrating polyelectrolytes. It has been found they do not penetrate into the PDMAEM·HCl gel. When a long contact (during a month or more) of PDMAEM·HCl gel with Na PSS (P_w=22 and 500), KPVS (P_w=700), or heparin aqueous solutions takes place, the concentration of linear polyions in the solution practically does not change and the gel volume remains constant. It is undoubtful, however, that very thin IPEC* layer is formed on the gel surface, which is the result of the IPAR. The existence of such a layer can be determined by the interference picture in the reflected light. But here the whole process is stopped, since the IPER (4)



$$-\overset{+}{N}H\,\overset{-}{O_3}S- \; + \; \overset{+}{Me}\,\overset{-}{O_3}S^{*}- \longrightarrow \overset{+}{Me}\,\overset{-}{O_3}S- \; + \; -\overset{+}{N}H\,\overset{-}{O_3}S^{*}- \qquad (4)$$

on the IPEC-gel inner interface in this case appears to be kinetically banned. The reason of this kinetic ban on the IPER (4) in these systems is not yet clear. It can only be mentioned that the IPECs of linear polycations with polysulfate and polysulfonate anions are much more stable than those with polycarboxylate anions (Ref.18). Such thin IPEC* surface layer locks the PDMAEM·HCl gel completely from penetration of polycarboxylate anions.

CONCLUSION

The data and the considerations presented above can have fundamental value for modelling and understanding of physicochemical mechanisms of the regulated active transport of polyelectrolytes in biological media - in particular, in the cell matrix- and for design of various functional polyelectrolyte systems. The reactions between linear and cross-linked polyelectrolytes are in essence the selfassembly processes which can be used to design the "core-shell" type structures with controllable thickness of IPEC shell. Constructions of that kind are of interest for the creation, for instance, of controlled drug release systems and various diagnostic devices. These reactions allow to design the multilayer structures including nonmixible layers composed of different interpolyelectrolyte complexes with predetermined thickness and arrangement of alternative layers. The alternative layers can be include together with synthetic polyelectrolytes also the biological macromolecules, in particular, proteins (enzymes). IPECs incorporating cross-linked polyelectrolytes are interesting by themselves as membranes for the active and selective transport of linear polyelectrolytes (Ref.19).

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