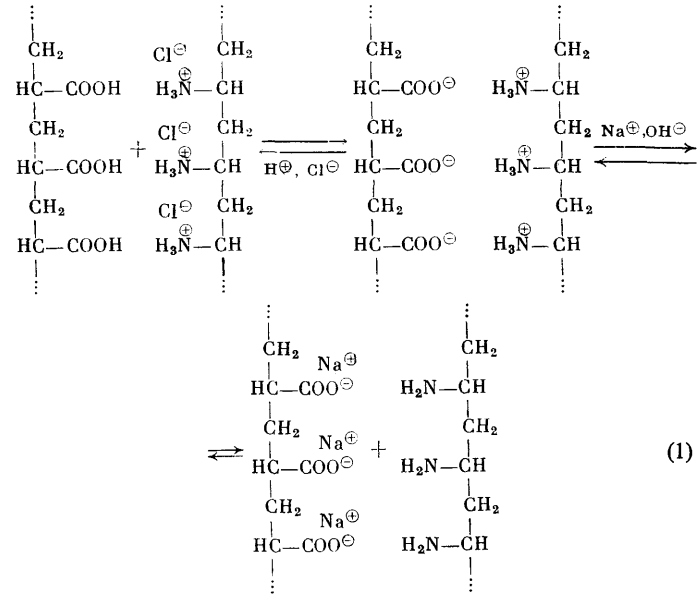
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Polyelectrolytes in the solution of ecological problems

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Polyelectrolytes have been used traditionally for the decomposition of colloidally disperse systems and for structure formation in the latter. We have shown in recent years that the use for such purposes of polymeric complexes formed by the interaction of two oppositely charged elecrolytes—polyelectrolyte complexes (PEC)—leads to qualitatively new possibilities in this field.

The interaction of linear polyelectrolytes bearing unlike charges is due to the occurrence of reversible reactions involving the formation of new bonds between chemically complementary units of the reacting molecules. The reaction between polyacrylic acid (PAA) and polyvinylamine (PVA) is illustrated schematically below:



(1)

Fig. 1 (curves *1* and *2*) illustrates the dependence of the degree θ of the interpolyelectrolyte reaction (1) on the pH of the reaction medium. The degree of reaction (1) is understood as the fraction of the units of the polymeric acid or base which have formed salt linkages with the units of the oppositely charged macromolecule, i. e.

$$\theta = c_k c_0,$$

where c_k = $[-COO^-H_3N^+-]$ is the concentration of the interpolyelectrolyte salt bonds and c_0 the concentration of the units of the polymeric acid or base in the reaction system. Evidently the degree of reaction (1) increases and reaches the high value θ = 0.8 within a narrow pH range (1–2) (curves *1* and *2*), while the degree of ionisation α of the corresponding weak polyelectrolytes (curves *3* and *4*) increases monotonically over a wide range of the pH of the reaction medium. This demonstrates the cooperative character of the interpolyelectrolyte reaction and the anticooperative character of the charging process involving free polymeric acids and bases. The cooperative nature of the interpolyelectrolyte reaction is responsible for the exceptionally high stability of the polyelectrolyte complexes within certain pH and ionic strength ranges. In such media, polyelectrolyte complexes are capable of swelling to only a limited extent and give rise to a kind of plastic hydrogel. At the same time, at salt, acid, or alkali concentrations exceeding critical values, the equilibrium in reaction (1) shifts to the left, the interpolyelectrolyte salt linkages holding together the polyions break, and the polyelectrolyte complexes are converted into a soluble state.

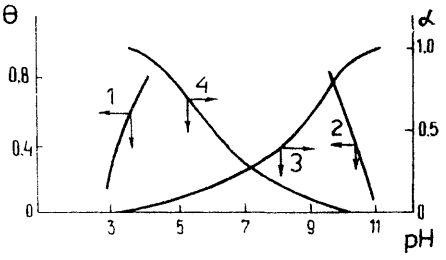
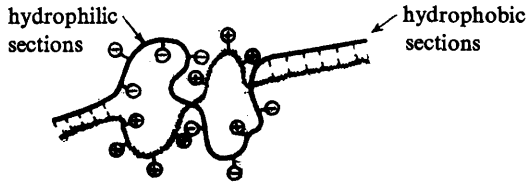
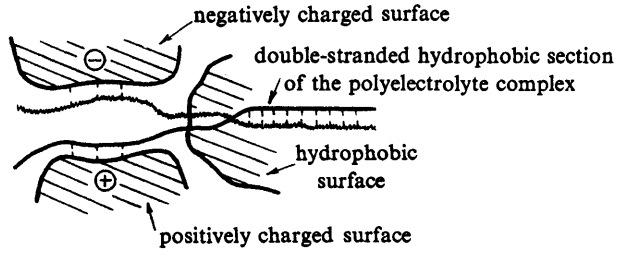


Figure 1. Dependence of the degree of the interpolyelectrolyte reaction θ between equimolar amounts of high-molecular-weight polyacrylic acid and polyvinylamine hydrochloride (curve *1*) and between sodium polyacrylate and polyvinylamine (curve *2*) on the pH. Dependence of the degree of dissociation α of polyacrylic acid (curve *3*) and polyvinylamine (curve *4*) on the pH. Concentration of polyelectrolytes 0.02 M; c_{NaOH} = 0.2 M; c = 0.1 M; t = 20 °C.

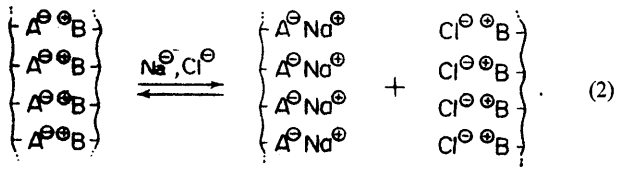
The polyelectrolyte complexes contain hydrophobic regions made up of paired sections of the complementary chains and hydrophilic sequences of ionogenic groups formed by disconnected sections of oppositely charged polyions. A fragment of a polyelectrolyte complex molecule is illustrated schematically below:



Sections of different nature in the swollen polyelectrolyte complex are capable of changing places with one another at a high rate. These structural features of polymeric complexes impart to the latter the unique capacity to be adsorbed on surfaces of different nature and to become adapted to varying external conditions in the contact zone. A fragment of a polyelectrolyte complex in contact with different particles of the disperse phase may be represented as follows:



The technology of the preparation and application of polymeric complex binders is extremely simple. It can be reduced to the preparation of dilute aqueous solutions of a mixture of polyelectrolytes in which the electrostatic interaction between oppositely charged polyions is prevented by shielding due to low-molecular-weight salts, for example, mineral fertilisers. The binder is then introduced into the disperse system, the solution being sprayed onto the surface of the soil or ground by means of any spraying technique. On subsequent washing of the treated layer with water, for example, by spraying or by rainfall, the shielding electrolyte is diluted and removed from the sphere of reaction (2):



(2)

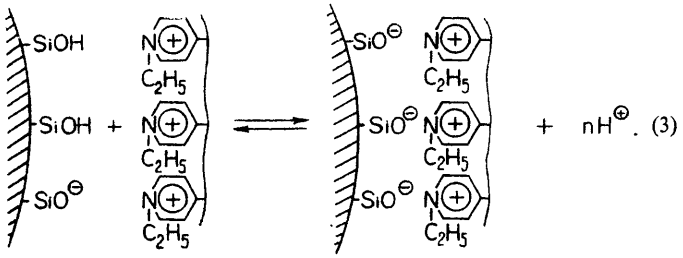
The equilibrium in reaction (2) is then displaced to the left, i.e. towards the formation of the polyelectrolyte complex. The resulting polyelectrolyte complex gel is capable of repeatedly drying out and becoming moist without impairment of adhesion properties, i.e. of the quality of the reinforced layer. Various low-molecular-weight organic and inorganic substances, for example, fertilisers, plant growth stimulators, herbicides, and other physiologically active compounds, can also be incorporated in the polyelectrolyte complex gels. For this purpose, it is sufficient to simply add them to the initial solution. The substances immobilised in the polyelectrolyte complex are then capable of being transferred from the polyelectrolyte complexes to the surrounding medium at a controlled rate.

By virtue of these properties, the polyelectrolyte complexes have been used successfully as structure-forming agents for soils to prevent their erosion by water and wind and to achieve a simultaneous increase in fertility. In the soil-polymer crust, the particles of the disperse phase are linked to one another by thin layers of the polyelectrolyte complex. Such crusts are not broken up by strong winds and rain. The procedures described have been applied successfully, for example, to grass over the sloping sides of earth channels. Polymeric complexes introduced onto the surface of the ground prevent its wind and water erosion during the period necessary for the growth and development of the grass cover. This makes it possible to tidy up reclamation systems incomparably more economically and effectively than can be done by traditional procedures. Polymeric complexes have also been widely tested as agents for the prevention of the washing away of soils and the subsequent crust formation on cotton seedlings and also as agents preventing the blowing away of the protecting banks in vineyards by hurricane force winds (up to 30–40 m s^{-1}).

It is significant that all these antierosion measures can be applied with a very low consumption of polymers (from 20 to 100 kg ha^{-1}). Simultaneously with the main effect, a marked stimulation of planned growth and development is observed. Treatment of cotton fields with polymeric complexes after sowing enhances the development of the root system and improves the capacity of the cotton plant for germination. This favourable effect of the polyelectrolyte complexes on germination can be to a large extent explained by the greenhouse effect of the soil-polymer crust, which retards the evaporation of moisture from the surface of the soil.

In the solution of ecological problems, one can use as polyelectrolytes both synthetic industrial polymers, for example poly(diallyldimethylammonium chloride) (commercial name—VPK-402), poly(dimethylaminoethyl methacrylate), hydrolysed polyacrylonitrile (HYPAN), as well as the products of the modification of natural polymers, for example, cellulose. The use of the waste from major industries for such purposes is especially attractive. For example, oxidised ligands, which are the products of the treatment of wood, can be used as polyanions. These water-soluble polymers, which pollute the environment, can be extracted quantitatively from the waste of the cellulose-paper plants in the form of an insoluble complex which can be used, in its turn, as a structure-forming agent.

Linear polyelectrolytes are capable of reacting effectively with oppositely charged colloid particles. We established that this interaction is described satisfactorily within the framework of the idea that there is cooperative electrostatic attraction between the units of the linear polyelectrolyte and the oppositely charged ionogenic groups distributed on the surface of the colloid particles. A reaction of this type between polysilicic acid (PSA) and the linear poly(*N*-ethyl-4-vinylpyridinium bromide) (QPVB) polycation is illustrated in Scheme 3. Reaction (3) results in the formation of polymer-colloidal polyelectrolyte complexes, whose composition is determined by the state of ionisation of the units of the linear polyelectrolytes and of the ionogenic groups distributed on the surface of the colloid particle:



(3)

Fig. 2 illustrates the dependence of the degree of the polymer-colloid reaction between the polyelectrolyte complex and QVPB on the pH (curve *1*). Evidently, as in the case of interpolyelectrolyte reactions, the formation of the polymer-colloid polyelectrolyte complex is accompanied by an appreciable increase in the degree of ionisation of the surface silanol groups of polysilicic acid (cf. curves *2* and *3*). It is seen from the above figure that the degree of reaction (3) in terms of the linear polymer (curve *1*) increases with increase in pH to the higher value (QPVB) = 0.7 at pH 9. This means that in alkaline media most of the units of the linear polycation are linked by salt bonds with the surface of the colloid particles. The relatively small steepness of the θ–pH curves, i.e. the low cooperativity of the polymer-colloid reactions is a consequence of the conformational non-complementarity of the interacting components—linear macromolecules and compact colloid particles. The conformation of the linear macromolecule, incorporated in the particles of the polymer-colloid polyelectrolyte complex, is characterised by the presence of a large number of loops. In other words, the set of its conformations is appreciably depleted compared with the set of conformations of a similar macromolecule in a dilute solution. A natural consequence of this is the tendency of the particles of the polymer-colloid polyelectrolyte complex to aggregate and form larger particles—floccules. Thus the flocculation of the colloid systems when the latter interacts with linear polyelectrolytes is in fact caused by the impairment of the thermodynamic quality of the solvent in relation to the chains linked to the surfaces of the colloid particles and hence by the spontaneous segregation of the adsorbed macromolecules as a concentrated phase. In the large

associated species (floccules) formed under these conditions, the colloid particles are separated from one another by polymer layers swollen to the maximum extent and formed by sections of the adsorbed polymer chains which on adsorption failed to come into contact with the surfaces of the colloid particles.

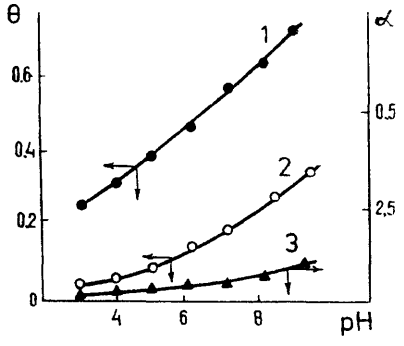


Figure 2. Dependence of the degree of the polymer-colloid reaction between QPVP and the polysilicic acid sol [*1*, θ(QPVP); *2*, θ(PSA)] and of the degree of dissociation of the surface silanol groups of the polysilicic acid sol (curve *3*) on the pH; c(QPVP) = 0.0025 M; degree of polymerisation of QPVP = 2500; sol particle radius = 56 Å; t = 20 °C.

By virtue of the ability of linear electrolytes to react with colloid particles, they are used as flocculants for the intensification of the processes involving the separation of highly disperse suspensions and emulsions. This is required, in the first place, for the creation of closed water circulation systems in undertakings of the mining industry. As an example, one may quote the successful use of the Soviet-produced industrial polycation VPK-402 in the Lovozersk mining-enrichment plant as a flocculant in connection with the establishment of a closed water circulation. The joint use of oppositely charged polyelectrolytes proved to be particularly effective. This makes it possible to reduce by an order of magnitude the consumption of polymer-flocculants with the simultaneous appreciable increase in the rate and quality of the clarification of dispersions. This was demonstrated in relation to the thickening of the highly disperse fraction of the ore from the Beloziminsk deposit (Fig. 3). Fig. 3 shows that the introduction of polymeric anions, for example HYPAN, hardly alters the rate of deposition of colloid particles (curve *1*). On the other hand, linear polycations play the role of flocculants (curve *2*). However, an increase in the content of VPK-402 above a certain optimum amount is again accompanied by a decrease in the rate of deposition and also in the quality of the clarification of the colloid system, i.e. under these conditions the polycation functions as a stabiliser of the disperse system. A qualitatively different flocculation picture is observed when linear polyelectrolytes bearing unlike charges are introduced jointly (curve *3*). In this case the rate of separation of the disperse phase is much higher than in the case where only the polycation is used and the effect indicated is attained with appreciably lower consumptions of the jointly applied oppositely charged polyelectrolytes compared with the cationic flocculant (cf. curves *2* and *3*). It is important to note that the high rate of deposition of the disperse particles and the quality of the clarification of the colloid systems persist over a wide range of variation of the concentrations of a polycomplex flocculant of this kind. In addition, this makes it possible to avoid the undesirable effects due to the partial stabilisation of dispersions on exceeding the dose of the flocculant.

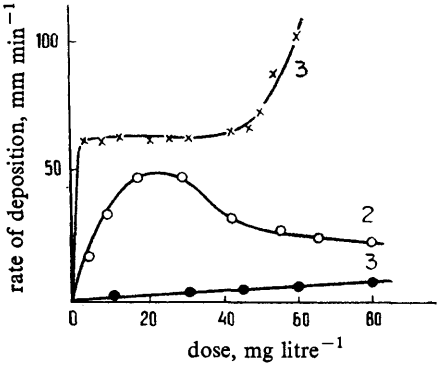
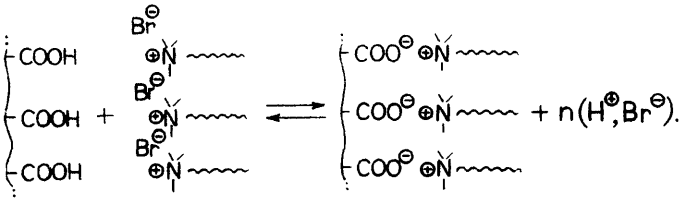


Figure 3. Flocculation of the sludge from the elutriation crust of the lanthanide ores from the Belozimsk deposit; sludge concentration 10 wt.%; particle size 70 μm: *1*, HYPAN; *2*, VPK-402; *3*, HYPAN; VPK-402 = 1:1.

Linear polyelectrolytes are able to interact cooperatively with oppositely charged micelle-forming surfactants. Such a reaction between polyacrylic acid and dodecyltrimethylammonium bromide (DDTMAB) is presented below:



(4)

As in the case of reactions between chemically complementary linear macromolecules, the polyelectrolyte—surfactant reaction is characterised by a high cooperativity (Fig. 4). The degree of such reaction increases sharply within a narrow range of the pH of the reaction mixture. The degree of dissociation of the polymeric acid incorporated in the polyelectrolyte complex particle then exceeds the degree of dissociation of the free polymeric acid at the same pH (cf. curves *1* and *2*). This results in the formation of stable polymeric polyelectrolyte—surfactant complexes stabilised by the hydrophobic interactions of the alkyl substituents in the surfactant with one another and with the hydrophobic sections of the chain in addition to the salt bonds formed between the ionogenic groups of the linear macromolecule and the diphilic surfactant ions. Such polymeric complexes are formed at a surfactant concentration in the solution lower by two and more orders of magnitude than the critical concentration for a micelle formation (CCM) for the same surfactant. This makes it possible to employ polyelectrolytes for the

effective extraction of surfactants from spent waters. The polymeric complexes isolated under these conditions are in their turn highly effective flocculants capable of decomposing simultaneously mineral dispersions and emulsions of organic substances. This has been demonstrated in experiments on the purification of spent waters in the rolling mills of the Moscow "Serp i molot" (Hammer and sickle) factory.

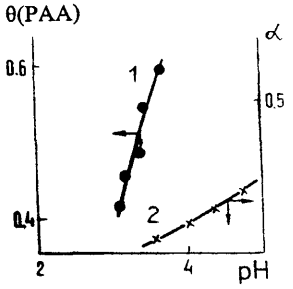


Figure 4. Dependence of the degree of reaction θ between equimolar amounts of polyacrylic acid and dodecyltrimethylammonium bromide (DDTMAB) (curve *1*) (polyacrylic acid and DDTMAB concentrations 0.03 M) on the pH; dependence of the degree of dissociation α of polyacrylic acid (curve *2*) on the pH; c_{NaOH} = 0.1 M; *1*, 20 °C.

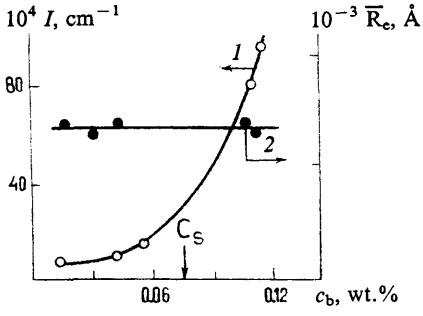


Figure 5. Dependence of the integral intensity of the scattered light *I* (curve *1*) and of the microemulsion drop size ($\bar{R}_e$) (curve *2*) on the amount of emulsified benzene (c_b); composition of the polyelectrolyte complex [PMANa]/[DDTMAB] = 0.2; [PMANa] = 0.03 M; [DDTMAB] = 0.03 M; pH 5.7; t = 20 °C.

The diphilic surfactant ions in the particles of such polymeric complexes are segregated into intramolecular micelles whose size and morphology are determined by the composition of the polymeric complex and the degree of polymerisation of the linear polyelectrolyte. By virtue of the presence of the intramolecular micellar phase, the polyelectrolyte–surfactant polymeric complexes effectively solubilise organic substances which are sparingly soluble in aqueous media, with formation of thermodynamically stable microemulsions of the "oil–water" type. Fig. 5 presents the dependence of the integral intensity of scattered light (curve *1*) and the drop size of microemulsions (curve *2*) on the amount of emulsified benzene. Eviently the size of the drops of the benzene microemulsion in water, stabilised by the complex of sodium polymethacrylate (PMANa) and the surfactant, is independent of the amount of emulsified benzene, while the integral light scattering intensity increases with increase in the amount of emulsified hydrocarbon. It is noteworthy that microemulsions are formed at a hydrocarbon concentration appreciably lower than that of the saturated solution of the hydrocarbon in water (c_s). This means that the drops of the microemulsion consist of a solution in the hydrocarbon of fragments of the polymeric acid bound to the aliphatic groups of the surfactant. The microemulsion particles can be readily separated from the aqueous medium, for example, by adding small amounts of polycations to the system. Thus the polymeric complexes of linear polyelectrolytes with micelle forming surfactants can be used to extract sparingly soluble organic compounds from aqueous media.

Polyelectrolytes have been used successfully also for the extraction of metal ions from aqueous media. Cross-linked polymers, capable of forming complexes with transition metal ions, including heavy metals, are widely used for this purpose. It has been found that the degree and rate of extraction of the metal can be increased by an order of magnitude by using a simple but effective method of "adjusting" the polymeric sorbent to a particular ion. This procedure consists in the fixation of the optimum conformations of the sections of the chains which arise in the polymer-metal complex formed by the linear polyelectrolyte. The complex is then cross-linked. The resulting complex-forming cross-linked polymer "remembers" the optimum structure and in subsequent cycles behave as an "adjusted" highly effective polymeric sorbent.

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New metal- and carbon-containing catalysts for the catalytic removal of harmful impurities from industrial gaseous waste

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The intensification of economic activity has led in recent years to dangerous ecological complications in many regions of our country. Emission into the atmosphere of gaseous waste comprising nitrogen and carbon oxides, carbon disulphide, organic sulphides, hydrogen cyanide, ammonia, and acetylene, which are present in the industrial waste from chemical, petrochemical, gas, and metallurgical industries, in automobile exhausts, in the exhausts from thermal power stations, etc., has given rise to especially great fears.

The incorporation in the processing treatment and the increase in the degree of utilisation of new types of petroleum, gas condensites, and accompanying gases with a high content of hydrogen sulphide and mercaptants are characteristic of the petroleum processing and gas industries in the USSR. For example,