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The properties of solutions and complex formation reactions of amphoteric polyelectrolytes

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ABSTRACT. The review presents the experimental results of studies on the physicochemical and complex-forming properties of synthetic polyampholytes in dilute solution. The similarity of the behaviour of polyampholytes at the isoelectric point and polyelectrolyte complexes is demonstrated. Questions concerning the complex formation reactions of polyampholytes with inorganic and organic ions, polyelectrolytes, and proteins are discussed. The role of competing interactions in the formation of intramolecular and intermolecular polycomplexes is considered.

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I. Introduction

Polyampholytes belong to the class of polyelectrolytes containing acid and basic functional groups in the macromolecule.[1–8] They can include chains with strongly and weakly acidic or strongly and weakly basic groups in various combinations.[9–12] Depending on the type of distribution of the acidic and basic units in the chain, polyampholytes can have a statistical, alternating, graft, and block structure.

The interest in the study of polyampholytes is determined primarily by the fact that they include the most important natural polymers—proteins and nucleic acids.[13] Biopolymers have a specific structure, function, and properties, which are fully realised only in a living organism.[14] Nevertheless a series of individual properties of natural polymers can be modelled with the aid of their synthetic analogues.[15]

The question of the association of polyelectrolytes with high-molecular-weight and low-molecular-weight substances of different nature constitutes the basis of processes occurring in the organism such as replication of the DNA strands, denaturation of biopolymers, protein–lipid interactions, enzyme catalysis, etc. By virtue of the high content of ionogenic groups in the chain, polyampholytes have found extensive practical application as flocculants, complexones, polymeric catalysts, agents prolonging the action of medicinal preparations, semipermeable membranes, artificial vaccines, etc.[16–20]

In the present review, an attempt is made to analyse the experimental data accumulated in recent years in order to discover the prospects for the development and the possible applications of this interesting class of macromolecular compounds.

II. Characteristic features of the behaviour of synthetic polyampholytes in solution

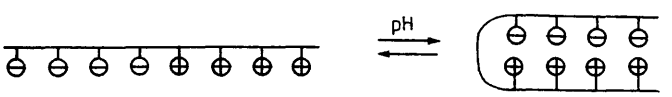
The behaviour of polyampholytes is determined both by the nature of their functional groups and by the features due to their macromolecular nature. Depending on the pH of the medium, they behave as polymeric acids or as polymeric bases and therefore exhibit the properties of homopolyelectrolytes. The pH at which the charge of the macromolecule is zero corresponds to the isoelectric point (IEP) of the polyampholyte.

It is assumed that in the vicinity of the IEP an appreciable proportion of the acid and basic units condense into a compact globule, displacing the solvent.[21] Hydrogen bonds and hydrophobic interactions can participate together with intra-ionic contacts in the stabilisation of such compact species.[22] The compactness of the macromolecules at the IEP can depend on the contributions of the above interactions.

The state of the polyampholyte species at the IEP is described satisfactorily by the "fringed globule" model, which has been analysed theoretically in detail by Lifshits et al.[23] As predicted previously by the theory,[24] the structural organisation of the globule presupposes the presence of two phase regions—a dense core from which almost the entire solvent has been displaced and fluctuating loop-shaped sections of the molecule present in the solvent and forming the fringe round the globule. This feature makes it possible to regard polyampholytes as convenient objects for the study of the phenomenon of collapse[25,26] and of the phase state of polymer molecules.[27]

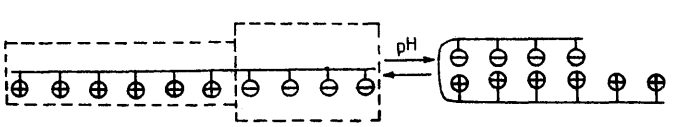
Information about the hydrodynamic and conformational properties of a series of amphoteric polyelectrolytes, soluble in the vicinity of the IEP, has been published.[28–37] The following features of the behaviour of synthetic polyampholytes of the IEP have been noted: (1) the "antipolyelectrolyte" effect, i.e. the increase in intrinsic viscosity with increase in the ionic strength of the solution; (2) the absence of intermolecular associated species (this is indicated by the similar average hydrodynamic molecular weights M_{η} calculated at different pH, including pH_{IEP}); (3) the anomalous dependence of the intrinsic viscosity on the molecular weight (in the Mark–Kuhn–Houwink equation, $a < 0.5$).

Polyampholytes with a block structure of the chains have a series of distinctive features, compared with the statistical and alternating analogues, due to the combination in the chain of long acidic and basic sequences. One of these features is the possibility of the formation of intramolecular polyionic complexes in the vicinity of the IEP. It has been shown for a diblock copolymer of sodium polystyrenesulphonate and poly-2-vinylpyridine[38] that the conformation of the macromolecules changes as a function of the degree of ionisation of the vinylpyridine blocks in the following manner: in the uncharged state ($\beta = 0$), they have a "segregated" structure with a core made up of vinylpyridine blocks maintained in water by the polystyrenesulphonate block; for low values of β, the structure consists of a coil "frozen" by rare ionic cross-links; for $\beta = 0.86$ (IEP), the macromolecules have the compact structure of a polyelectrolyte complex (PEC) stabilised by the cooperative interactions of the acidic and basic blocks. Polyelectrolyte complexes were also formed at the IEP by block copolymers based on poly-1-methyl-4-vinylpyridinium methochloride and polymethacrylic acid (P1M4VP-PMAA).[38] For example a broad region of insolubility (ΔpH ~3.5) in water is characteristic of P1M4VP-PMAA with an equimolar composition, the region becoming appreciably narrower and ultimately vanishing completely with increase in the ionic strength of the solution (Fig. 1). The precipitation of P1M4VP-PMAA in the vicinity of the IEP is evidently associated with the formation of an intramolecular stoichiometric PEC (S-PEC) as a result of the coooperative interaction of the acidic and basic blocks.



The dissolution of P1M4VP-PMMAA at a high ionic strength is caused by the decomposition of the S-PEC species as a result of the shielding of the oppositely charged units of the block polyampholyte by low-molecular-weight ions.

Block polyampholytes containing an excess of the acidic or basic block can be fully classified as intramolecular non-stoichiometric PEC (N-PEC). The relatively long cationic or anionic blocks can play the role of the lyophilising polyelectrolyte (LPE) in this instance, while the role of the blocking polyelectrolytes (BPE) is assumed by short acidic or basic blocks.



Such N-PEC species are maintained in solution and their precipitation is prevented by the hydrophilic fringe, consisting of unreacted cationic or anionic blocks. Calculation of the degree of conversion† in the N-PEC formation reaction showed that the process has a cooperative character.[39]

† The degree of conversion θ is the fraction of the intramolecular or intermolecular salt bonds formed relative to their maximum possible number.

III. Association of polyampholytes with transition metal ions, dyes, and surfactants

The study of the polyampholyte–metal complex formation processes is of interest from the standpoint of bioorganic chemistry.[40,41] A quantitative characteristic of the strength of the binding of metal ions to macromolecular ligands is the formation constant or the so-called formation function proposed by Bjerrum.[42]

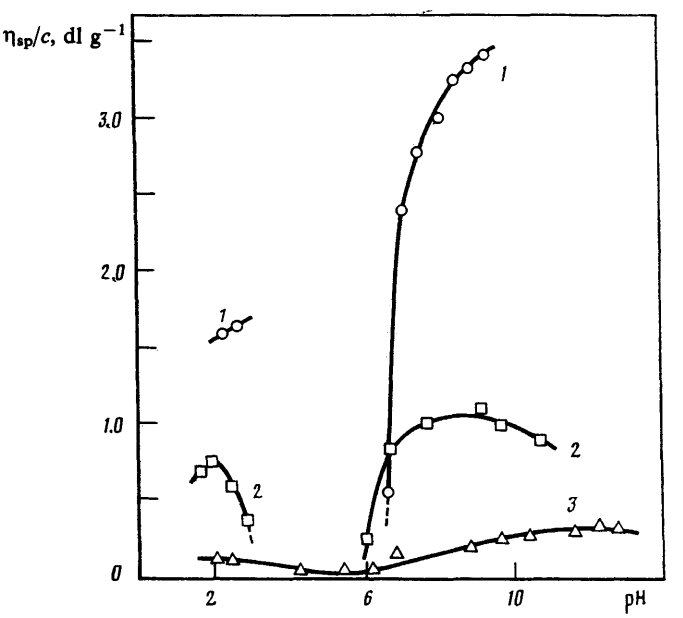
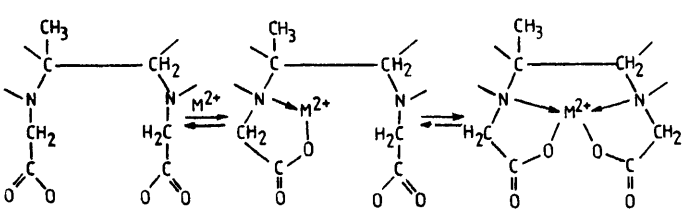


Figure 1. Dependence of the intrinsic viscosity of solutions of the block polyampholyte based on poly-1-methyl-4-vinylpyridinium methochloride and polymethacrylic acid (45:55 mol.%) on the pH in water (curve *1*) and in the presence of 0.01 M (curve *2*) and 0.3 M KCl (curve *3*); c_{BPA} = 0.045 g dl^{-1}.

Multidentate polyampholytes have been synthesised[43] and their chelating properties have been investigated. The polyampholytes react with metal ions in two stages:



As a consequence of the formation of five-membered rings, the polyampholyte–metal complexes have high stability constants. The stability of the chelate compounds varies in the sequence Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Pb^{2+} > Fe^{2+} > Ca^{2+} > Mg^{2+}. It

identical with the stability series of the complexes of the same metals with EDTA.[44]

Depending on the pH of the medium, amphoteric polyelectrolytes are capable of forming several types of complexes with participation of carboxy- or amino-groups and also complexes of a mixed type.[8] The binding of Ca^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} ions by polyampholytes based on *N,N*-dimethylaminoethyl methacrylate and methacrylic acid (DMAEM-MAA) has been investigated by the potentiometric method.[45] The Mg^{2+} ion formed a stable complex at pH > 9.7, while Co^{2+} was bound to DMAEM-MAA in the range 7.5 < pH < 9.5. The formation of Cu^{2+} and Zn^{2+} complexes was observed in the region of pH 5.8 and 7.4 respectively. The Ca^{2+} ion showed no complex-forming capacity at any pH.

On the basis of theoretical studies and the intermolecular cross-linking of macromolecules, Plate et al.[46] were able to predict the principal characteristics of the complex formation reaction between macromolecules and metal ions in relation to the interaction of poly-N^{ε}-methacryloyl-*L*-lysine (PML) with copper(II) ions. Comparison of potentiometric titration, UV spectroscopic, and equilibrium dialysis data shows that at pH > 4.5 copper ions are bound to two lysine residues of PML. Two monomeric units of one macromolecule are involved predominantly in the process. Such a process is an example of an intramolecular cross-linking reaction.

In order to identify the structure of the copper complexes of aminocarboxypolyampholytes, the EPR spectra of the latter were compared[47] with those of copper–glycine and copper–alanine complexes. It was shown that the complexes formed in the amino-acid solutions at pH > 3 are analogous to the complexes in aminocarboxy-resins. Depending on the pH of the medium, copper ions are coordinated predominantly to carboxy-groups or carboxy- and amino-groups of the polyampholytes. The fraction of the structure of each type is determined by the pH of the solution.

Analysis of the EPR spectral lines for the 2-methyl-5-vinyl-pyridine-acrylic acid/copper(II) (2M5VP-AA/Cu^{2+}) complex revealed two types of spectra differing by the parameters $g_{\perp}$, $g_{\parallel}$, and $A_{\parallel}$.[48,49] In an acid medium, the signal characteristic of the type "A" structure with the parameters $g_{\perp} = 2.058$, $g_{\parallel} = 2.334$, and $A_{\parallel} = 136 \times 10^{-4}$ cm^{-1} predominates in the spectrum. On passing to the neutral region, the intensity of this line gradually falls and is replaced by an increase in the intensity of the EPR signal of a complex of another type (type "B") with the parameters $g_{\perp} = 2.035$, $g_{\parallel} = 2.298$, and $A_{\parallel} = 157 \times 10^{-4}$ cm^{-1}. Bearing in mind the similarity of the parameters of the "A" spectrum to those of the spectrum of the copper complex with polyacrylic acid and copper acetate, one may conclude that in an acid medium the carboxy-groups of the acrylic acid units are predominantly coordinated around the copper ions. The dependence of the average coordination number $\bar{n}$ on the pH of the medium shows that the formation of the complex ML_2 is completed at pH < 6.0. The higher value of $A_{\parallel}$ and the lower value of $g_{\perp}$ for the EPR signal in the spectrum of the "B" complex show that the coordination environment of copper includes, apart from two carboxy-groups, two pyridine units. These results permit the conclusion that a complex with $\bar{n} = 2$ and $\lg\beta = 13.5$ is formed at pH < 6.0, while a complex with $\bar{n} = 4$ and $\lg\beta = 21$ is formed in the range 6.0 < pH < 10.0.

A similar rearrangement of the coordination sphere of copper ions has been observed also for ternary polymer–metal complexes (TPMC), which have been examined in detail.[50–52] In particular, it was noted that two types of structures (A and B), differing in the structure of the coordination sphere of the central ion, are characteristic of the products of the interaction of polyacrylic acid (PAA), linear polyethyleneimine (PEI), and copper(II) ions. At high pH, the amino-groups of PEI are not protonated and the complex $Cu(PEI)_2^{2+}$ with a type A structure is mainly formed. As the pH is reduced, the nitrogen atoms of the PEI ligand are protonated and the fraction of the type A structure begins to diminish with the simultaneous increase in the fraction of the type B structure, in which one of the two amino-groups in the coordination sphere is replaced by two carboxylate ions of PAA: $(CuPEI)(PAA)_2$. Thus in this case too the number and type of functional groups of the polyampholytes in the coordination sphere of the metal ion are determined by the pH of the medium.

In the course of the study of the complex-forming properties of synthetic polyampholytes, we observed that polyampholytes based on piperidinol derivatives[53,54] are capable of binding metal ions at certain pH values and of liberating them strictly at the IEP. The principle of the action of polyampholytes at the IEP is apparently that, after the attainment of pH_{IEP}, the cooperative interaction forces between the acidic and basic groups become more effective, which leads to the "expulsion" of the previously bound metal ions from the bulk of the coil of the macromolecule. If the IEP of the polyampholyte is located in the alkaline region, then transition metal ions are precipitated while the polyampholyte remains in solution and can be regenerated and used anew. In this sense, the behaviour of polyampholytes at the IEP resembles that of TPMC.[50–52] For example, at certain pH values the nitrogen–metal coordinate bonds and carboxylate–metal ionic bonds in the polyethylene-imine–metal–polyacrylic acid system are replaced by cooperative polycation–polyanion salt contacts.[55] In contrast to the ampholyte, the PEC is then precipitated, while the metal ions remain in solution.

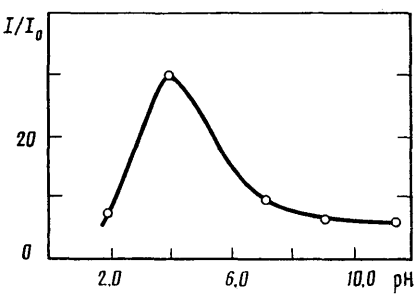


Figure 2. Dependence of the relative fluorescence intensity of 1-anilinonaphthalene-8-sulphonic acid on the pH in the presence of the 2,5-dimethyl-4-vinylethynyl-4-piperidinol–acrylic acid copolymer (DMVEP:AA = 45.2:54.8 mol.%); [DMVEP-AA]:[ANS] = 100:1; [ANS] = 5 × 10^{-5} M.[57]

The available literature data concern in the main the association of polymeric acids, polymeric bases, and non-ionic polymers with dyes and surfactants.[56] On the other hand the data obtained in studies of the interaction of synthetic polyampholytes with dyes and surfactants are virtually lacking. The results of the investigation of the dependence of the intensity of the fluorescence of 1-anilino-naphthalene-8-sulphonic acid (ANS) (I/I_0) in the presence of the polyampholyte over a wide pH range are presented in Fig. 2.[57] The

greatest increase in the intensity of the fluorescence of the dye is observed at pH 3–3.5, i.e. in the region of the intense ionisation of the basic groups of the polyampholyte. The sharp decrease of I/I_0 from 30 to 4 in the vicinity of the IEP of the polyampholyte (pH_{IEP} = 7.0) indicates the decomposition of the polyampholyte–ANS complex and the appearance of free dye molecules. The dye is liberated similarly after the addition of polyacrylic acid to the polydiallyldimethylammonium chloride–ANS system, as a consequence of the competing effect of the second macromolecular component.[58]

The mechanism of the "expulsion" of ANS at the IEP of the polyampholyte is apparently similar to the mechanism of the expulsion of the metal from the polyampholyte–metal system examined above.

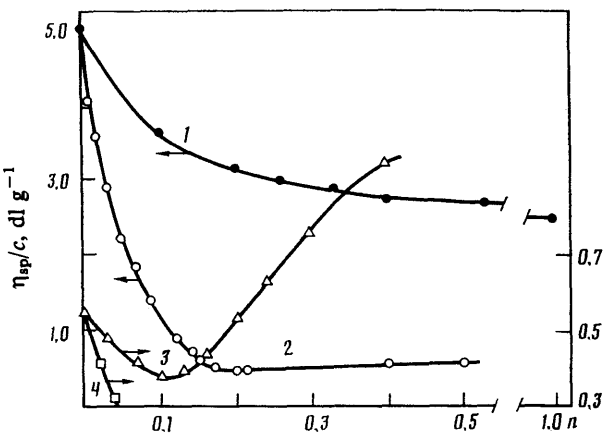


Figure 3. Dependence of the intrinsic viscosity of solutions of polyampholytes based on 1,2,5-trimethyl-4-vinylethynyl-4-piperidinol and acyrlic acid (TMVEP : AA = 40 : 60 mol.%) (curves *1* and *2*) as well as styrene and *N,N*-dimethylaminopropylmonoamide of maleic acid (S : DMAPMAMA = 50 : 50) (curves *3* and *4*) on the [surfactant]/[polyampholyte] = *n* molar ratio; [TMVEP-AA] = [S-DMAPMAMA] = 1×10^{-2} M.[59–61]

Synthetic polyampholytes have the ability to bind cooperatively anionic and cationic surfactants undergoing at the same time appreciable conformational changes.[59–62] The binding of anionic and cationic detergents by polyampholytes takes place mainly via electrostatic interaction, while the compact polymeric complex species is stabilised by the hydrophobic interactions of the long alkyl components of the surfactant and is maintained in solution and its precipitation is prevented by the hydrophilic components of the copolymers which have not been involved in the complex.[59–62] Fig. 3 illustrates the influence of sodium dodecyl sulphate (DDS) and cetyltrimethylammonium chloride (CTMA) on the hydrodynamic dimensions of the molecules of polyampholytes. The decrease in the intrinsic viscosity η_{sp}/c in the presence of surfactant is evidently associated with the formation of ampholyte–surfactant polymeric complexes. The results of the calculation of the degree of conversion in the formation reaction of the polyampholyte–surfactant complexes shows that the polymeric complexes are formed within a narrow pH range, which indicates the cooperative nature of the process.

In contrast to a statistical polyampholyte, the styrene–maleic acid, *N,N*-dimethylaminopropylmonoamide copolymer (S–MADMAPMA), with a regular structure, contains, together with hydrophilic groups, also styrene units (50 mol.%), which can intensify the hydrophobic interactions between the non-polar units of the copolymer and the hydrocarbon components of the surfactant. This feature of S–MADMAPMA is clearly manifested in relation to CTMA and DDS. The addition of even an insignificant amount of CTMA induces a sharp decrease in viscosity as far as the formation of an insoluble deposit. This is caused by the marked conversion of the macromolecules into a hydrophobic form, which leads to the formation of globular polymeric complex species. On titration of the same copolymer with DDS, the viscosity of the system passes through a minimum. This form of the viscometric curve can be accounted for by the fact that initially the detergent molecules are bound electrostatically by the polyampholyte which results in the formation of an intramolecular micelle-like structure, giving rise to a more coiled conformation of the polymer coils. Subsequently additional adsorption of surfactant molecules on the polymer chains takes place, which leads to charge transfer in the macromolecules and to the swelling of the polyelectrolyte.

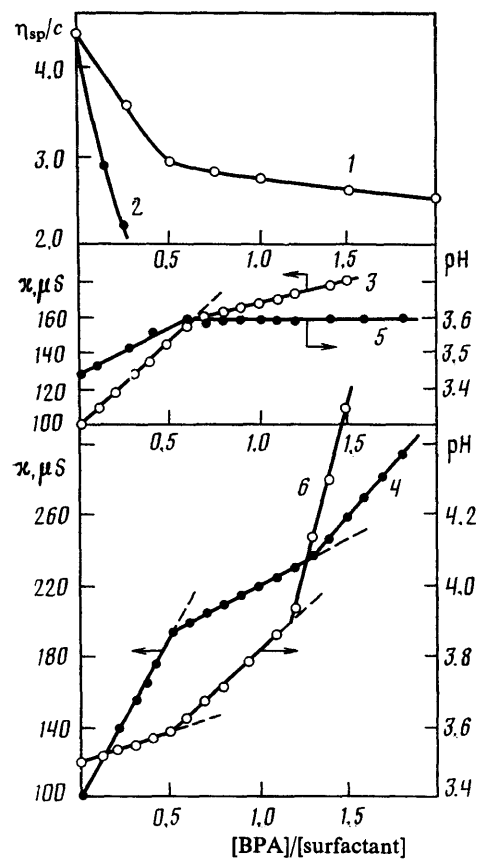
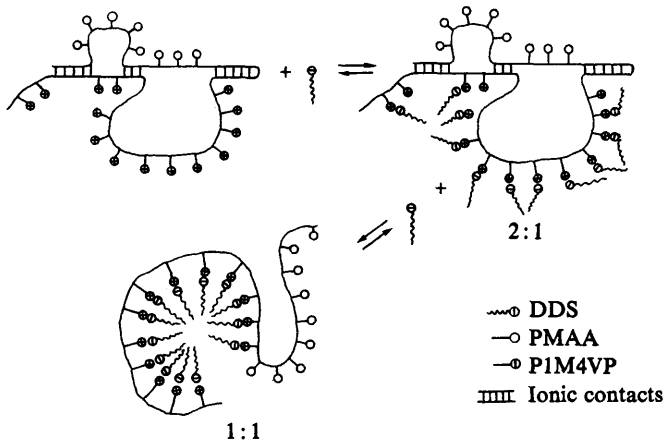


Figure 4. Viscometric (curves *1* and *2*), conductimetric (curves *3* and *4*), and potentiometric (curves *5* and 6) titration curves for a block polyampholyte based on poly-1-methyl-4-vinylpyridinium methochloride and polymethacrylic acid (64 : 36) the [BPA]/[surfactant] molar ratio: *1*, *3*, and *5*, [BPA]–[CTMA]; *2*, *4*, and *6*, [BPA]–[DDS]; [surfactant] = 5×10^{-2} M.

On potentiometric and conductimetric titration of an aqueous solution of a block polyampholyte (BPA) with a DDS solution, the formation of complexes with the ratios [BPA]:[DDS] = 2:1 and 1:1 was observed (Fig. 4). Initially only half of all the vinylpyridinium units enter into the reaction. On further addition of the ionic surfactant, the composition of the complex approaches the equimolar composition, which indicates the binding of an additional amount of DDS. It was shown previously by the luminescence quenching method[63] that micellar surfactants containing sulphogroups can compete with polymeric acids in polymeric complex formation reactions with linear synthetic polymeric cations. Consequently the mechanism of the interaction of BPA and DDS can be considered within the framework of competing reactions which occur in N-PEC/surfactant systems.[63] The formation of a 2:1 polymeric complex can be accounted for by the interaction of DDS with longer and shorter sections of the cationic block which do not enter into the formation reaction of the intramolecular N-PEC. The formation of the stoichiometric 1:1 polymeric complex is apparently due to the breakdown of the cooperative ionic contact between the acid and basic blocks ($COO^- - \overset{+}{N}$) and their replacement by cooperative ionic contacts ($SO_3^- - \overset{+}{N}$). Taking into account these considerations, the competing reaction of the anionic surfactant and BA can be represented schematically in the following way:



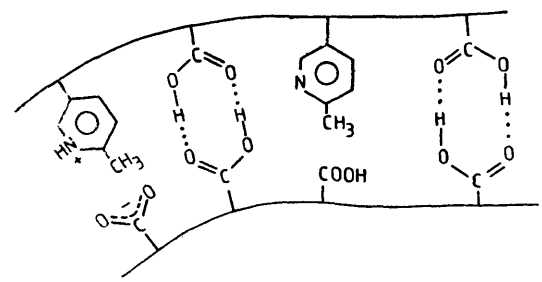
However, after the addition of a cationic surfactant, namely CTMA, to a solution of BPA, only an inflection corresponding to the 2:1 composition of the polymeric complex is observed on the potentiometric, conductimetric, and viscometric titration curves. This can be explained by the fact that the ionic contact with participation of the cationic surfactant cannot compete with the cooperative ionic contacts between the acidic and basic blocks, while the surfactant reacts only with the PMAA "loops" which constitute the "fringe" (see the scheme above). Thus the behaviour of the anionic surfactant–BPA system can be described satisfactorily on the basis of data obtained for the DDS–N-PEC system.[63]

It is of interest to trace the influence of organic additives on the behaviour of associating polyampholyte–surfactant systems.[59–62] In the case of the polyampholyte–DDS polymeric complex, a sharp increase in viscosity within a narrow range of variation of the solvent composition (in the range from 60 to 80 vol.% of methanol) was observed on the curve relating the intrinsic viscosity to the composition of the methanol–water solvent. In the remaining regions (above 80 and below 60 vol.% of methanol), the viscosity changes only slightly as the methanol content in the mixture is varied. These results can be interpreted in the following way. In pure water, the polymeric complex species acquire a compact structure stabilised by hydrophobic interactions. It persists up to a methanol content in the mixture of 60 vol.%. Further increase in the fraction of the alcohol induces a sharp increase in viscosity, which indicates the cooperative uncoiling of the compact structure as a consequence of the solvation of the hydrophobic components of the polymeric complex by methanol and of the hydrophilic components by water. In the latter case, we are dealing with an inverted micelle, which is formed as a result of the "precipitation" of the hydrophilic components of the copolymer by methanol. Thus the transition from one compact structure to another takes place via a stage involving rearrangement of the structure of the polymeric complex.

IV. Interpolyelectrolyte reactions with participation of synthetic polyampholytes

Considerable experimental data have accumulated hitherto on complex formation between synthetic polyelectrolytes. There have been surveys in a number of communications.[64–71] However interpolymer reactions with participation of synthetic polyampholytes have been studied very inadequately. Synthetic polyampholytes have the ability to bind cooperatively to both anionic (or cationic) and amphoteric macromolecules. Earlier Morawetz and Hughes[72] investigated the association of human serum albumin with the TMAEM–MAA copolymer. Kabanov et al.[73] investigated by potentiometric titration and turbidimetric methods the reactions between amphoteric 2M5VP-AA copolymers of different composition and PAA (5,6-ionene). The maximum turbidity of the system is observed in the pH range where the components are linked by the maximum possible, under the given conditions, number of ionic contacts and hydrogen bonds.

The stoichiometry of the 2M5VP-AA/PAA complex is independent of the composition of the copolymer and is 1:1. In contrast to the polyampholyte–polymeric acid system, 5,6-ionene forms a weak complex with the polyampholyte. According to the authors,[73] this is due to the impossibility of the formation in the polyampholyte–ionene system of a single cooperative sequence of ionic and hydrogen bonds between the interacting chains. The proposed structure of the polyampholyte–PAA polymeric complex can be represented as follows:



Interpolyelectrolyte reactions with participation of a sulpho-derivative of chitosan—a polyampholyte containing amino- and sulpho-groups in the chain—have been examined.[74] Fig. 5 presents curves for the turbidimetric titration of a solution of 2,5-ionene bromide with a solution of chitosan sulphate at pH 2.5 and 11.5. Evidently the compositions of the polyelectrolyte complex in the acid and alkaline regions differ significantly. In the acid region, only half of the OSO_3^- groups of chitosan sulphate ($Z' = 2$) participate in the formation of the polyelectrolyte complex. The remaining groups are incorporated in zwitter-ionic pairs with the amino-groups of a neighbouring glucoside ring. In an alkaline medium, the polyelectrolyte complex has the equimolar composition ($Z' = 1$), i.e. virtually all the sulpho-groups participate in the formation of the polyelectrolyte complex. In other words, as the pH of the medium is varied, there is competition between the formation of the zwitter-ions and the formation of the polyelectrolyte complex. The examples quoted above show that, by alternating the state of ionisation of the acidic and basic groups of polyampholytes, it is possible to vary within broad limits the composition and hence the structure and properties of the polyelectrolyte complex.

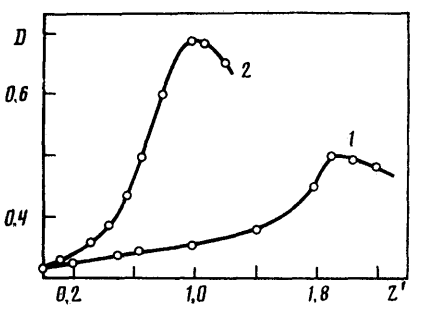


Figure 5. Curves for the turbidimetric titration of 2,5-ionene bromide with chitosan sulphate at pH 2.5 (curve *1*) and 11.5 (curve *2*); [2,5-ionene] = 5×10^{-4} M.[74]

The formation reaction of the polyelectrolyte complexes between synthetic polyampholytes (PAM) and polyacrylic acid was investigated previously[75] and the composition of the polymeric complexes was determined. The influence of the order of mixing of the polyelectrolyte components, the ionic strength of the solution, temperature, and the addition of an organic solvent on the composition and stability of the polyelectrolyte complexes was demonstrated.

The influence of the pH of the medium on the complex formation reaction between the equimolar 2,5-dimethyl-4-vinylethynyl-4-piperidinol–acrylic acid (DMVEP–AA) polyampholyte and PAA, polydiallyldimethylammonium chloride (PDADMAC), and human serum albumin (HSA) has been investigated.[76–78]

When aqueous solutions of polyelectrolyte components are mixed, the solution pH changes appreciably and this is accompanied by the appearance of turbidity in the system, which indicates the occurrence of the polyelectrolyte complex formation reaction. Fig. 6 illustrates the variation of the intrinsic viscosity of the polyelectrolytes and the polyelectrolyte complex as a function of the pH of the medium. The polyelectrolyte complex consisting of a polyampholyte and PAA is precipitated in the pH range from 3.0 to 5.5. The onset of the segregation of the reaction product as a separate phase corresponds to the onset of the ionisation of the amino-groups of the polyampholyte and to the partly ionised state of PAA. The dissolution of the polyelectrolyte complex in the strongly acid medium is apparently associated with its decomposition as a consequence of the suppression of the ionisation of the carboxy-groups of PAA and the formation of an ionic atmosphere around the positively charged nitrogen atoms caused by the excess inorganic acid. The precipitation of the polyelectrolyte complex consisting of a polyampholyte and polydiallyldimethylammonium chloride takes place at pH $\geqslant$ 8.2, i.e. with increase in the degree of ionisation of the carboxy-groups of the polyampholyte.

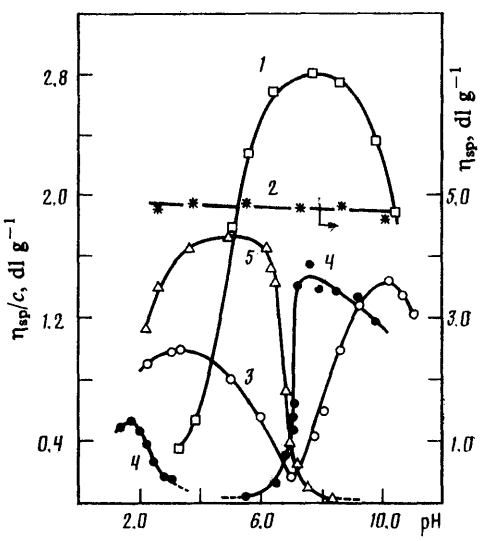


Figure 6. The influence of the pH of the solution on the intrinsic viscosity of polyacrylic acid (PAA) (curve *1*), polydiallyldimethylammonium chloride (PDADMAC) (curve *2*), the 2,5-dimethyl-4-vinylethynyl-4-piperidinol–acrylic acid copolymer (DMVEP : AA = 45.2 : 54.8) (curve *3*), and the polyelectrolyte complexes [DMVEP-AA] : [PAA] = 3 : 1 (curve *4*) and [DMVEP-AA] : [PDADMAC] = 3 : 1 (curve *5*); [DMVEP-AA] = 2.5×10^{-2} M.[77]

After the addition of human serum albumin to the polyampholyte, the quantity η_{sp}/c for the polyampholyte solution gradually diminishes, reaching a limiting value at $m_{HSA} : m_{PAM} = 3 : 2$. However, despite the appearance of a strong opalescence, phase separation does not take place in the system. The most favourable region of the interaction of the polyampholyte and human serum albumin corresponds to the pH range between their isoelectric points, since at these pH values the polyampholyte and human serum albumin macromolecules become positively and negatively charged respectively. The formation of a polyelectrolyte complex between the polyampholyte and human serum albumin apparently takes place as a result of the "adhesion" of more or less long sections of the polyampholyte chain to the surface of the

negatively charged protein globule.[79] It has been noted[80] that, on mixing aqueous solutions of natural polyampholytes—β-lipoprotein and γ-globulin—the formation of the polyelectrolyte complex is also observed. As in the interaction of a polyampholyte and human serum albumin, here the maximum degree of salt formation between the β-lipoprotein and γ-globulin takes place in the pH range between their isoelectric points.

There are literature data showing that the complexes of carbochain linear polyampholytes with proteins exhibit reduced immunogenic properties.[20] It has been found that the stability of the complexes formed depends on the composition of the 2-methyl-5-vinylpyridine–acrylic acid copolymer. According to the authors, hydrogen bonding and hydrophobic interactions play a decisive role in the formation of the polyampholyte–protein complex. However, against their background there is also a possibility of the formation of salt bonds by virtue of the induced ionisation of the corresponding ionogenic groups.

Thus the results obtained fully confirm the conclusion that[73] synthetic polyampholytes are capable of cooperative binding to both anionogenic or cationogenic and amphoteric molecules, differing significantly from homopolymers by the width of the spectrum of cooperative interactions.

Attention should be drawn to one of the characteristic features of the polyampholyte–polyelectrolyte complex, namely the sharp increase in viscosity occurring at the isoelectric point of the polyampholyte (pH_{IEP} 7.0) (Fig. 6). This phenomenon, which we called the "expulsion effect", occurs following a change in the pH of the medium induced by the coil–globule conformational transition in the polyampholytes. The process mechanism is apparently as follows.

Since the structure of the polyampholyte–polyelectrolyte complex consists of a double-stranded pair sequences formed by a single cooperative system of ionic and hydrogen bonds and also of defects of the loop ("fringe") type, it follows that, as the isoelectric point is approached, the cooperative interactions between the acidic and basic units of the polyampholyte, leading to the formation of intramolecular polyelectrolyte complexes (IAPEC), ultimately cause the decomposition of the polymeric polyampholyte–polyelectrolyte complex into individual components. The main driving force of the polyelectrolyte decomposition process at the isoelectric point of the polyampholyte is evidently the decrease in the Gibbs free energy as a consequence of the increase in the entropy of the system.

In order to demonstrate the cooperative nature of the decomposition of the polyelectrolyte complex species, sedimentation measurements were made. Fig. 7 illustrates the sedimentation diagrams for the 2,5-dimethyl-4-vinylethynylpiperidinol–acrylic acid (DMVEP-AA) polyampholyte, PAA, and the polyelectrolyte complex at different pH. At pH 6.1 and 6.9, a single peak with S = 4.75 and 4.18 Svedberg units can be seen on the sedimentogram. This shows that under these conditions the sedimenting particles are those of the polymeric complex. However, at pH $\geqslant$ pH_{IEP} (pH_{IEP} 7.0) two peaks appear on the sedimentogram with sedimentation coefficients of 1.9 ("slow" peak) and 5.6 Svedberg units ("fast" peak). Under identical conditions, the individual components have S = 1.06 (PAA) and 3.53 Svedberg units (DMVEP-AA). The appearance of the slowly and rapidly sedimenting particles within a fairly narrow pH range (ΔpH = 0.2) can be attributed to the cooperative decomposition of the polyelectrolyte complex species. However, in the presence of a low-molecular-weight salt, the cooperative nature of the decomposition is less marked. This is associated with the fact that the low-molecular-weight electrolyte leads to the shielding of the charges on the macromolecule and the loosening of the compact polyampholyte particles at the isoelectric point.

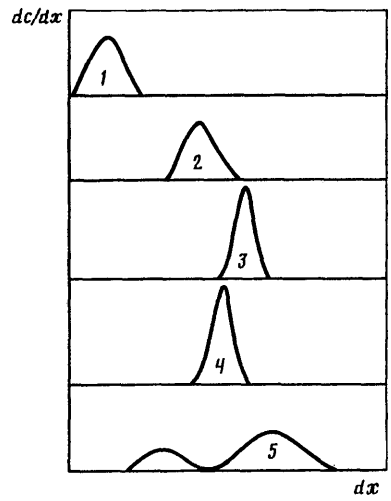


Figure 7. Sedimentograms for PAA (curve *1*), DMVEP-AA (curve *2*), and the [DMVEP-AA]:[PAA] = 3:1 polymeric complex (curves *3*–*5*) at different pH of the solution. Rate of rotation of the rotor 40,000 rev min^{-1}, T = 298 K, I = 0.005, τ = 60 min; pH: *1*, and *2*, 7.2; *3*, 6.1; *4*, 6.9; *5*, 7.1.

Polyampholytes with a block chain structure are capable of binding macromolecules with a more pronounced cooperative behaviour, in contrast to statistical and alternating polyampholytes.[39] The interpolymer complexes formed under these conditions can be stabilised by both ionic and hydrogen bonds. The compositions of the complexes, found from conductimetric, potentiometric, and viscometric titration curves, correspond to BPA:PAA = 1:1, where PAA may also be polybenzyltrimethylvinylammonium chloride (PBTMVAC), polyallyldimethylammonium chloride (PADMAC), or polyvinylpyrrolidinone (PVPD), and BPA:PEG = 2:1 (Fig. 8).

Calculation of the degree of conversion θ in the polyelectrolyte formation reaction between the block polyampholyte and an anionic (cationic) polyelectrolyte shows that the process is cooperative (Fig. 9, curves *1* and *2*). It is also noteworthy that the block polyampholyte is capable of forming a ternary polyelectrolyte complex by becoming "loaded" with cationic and anionic polyelectrolytes. However, the cooperative nature of such a reaction is less marked than that of the reaction quoted above, which is associated with the conversion of the macromolecules of the initial polyelectrolyte complexes into a compact form (Fig. 9, curve *3*). At the isoelectric point of the block polyampholyte, there is also a possibility of the existence of cooperative ionic contacts between the acid and basic blocks, leading to the formation of intramacromolecular polyelectrolyte complexes (Fig. 9, curve *4*). This justifies the assumption that, as the isoelectric point of the block polyampholyte is approached, the alternative possibilities of intramacromolecular and intermacromolecular

complex formation reactions may arise. If the first reaction is more cooperative than the second, then one cannot rule out the possibility of the decomposition of the interpolyelectrolyte complex and the formation of an intramolecular polyelectrolyte with subsequent liberation of the sorbed polyelectrolyte.

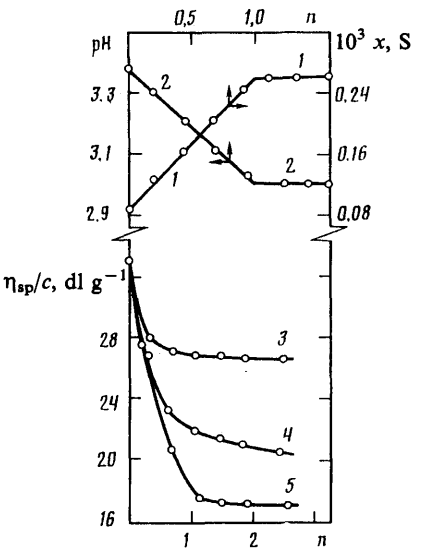


Figure 8. Variation of the electrical conductivity (curve *1*), pH (curve *2*), and intrinsic viscosity (curves *3*–*5*) with the molar ratio of the components *n*; *n*: *1*, and *2*, [BPA]/[PAA]; *3*, [BPA]/[PEG]; *4*, [BPA]/[PADMAC]; *5*, [BPA]/[PVPD].[39]

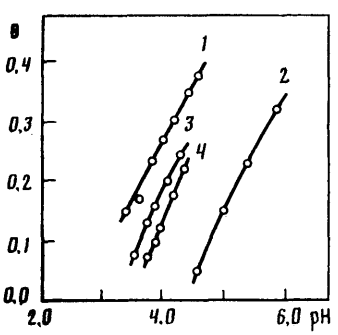


Figure 9. The profile of the dependence of θ on the pH for the BPA–PAA (curve *1*), BPA–PADMAC (curve *2*), and (BPA-PADMAC)–PAA (curve *3*) systems. Curve *4* corresponds to the formation of an intramolecular polyelectrolyte complex.[39]

The cooperative decomposition of the polyelectrolyte complex species at the isoelectric points of polyampholytes resembles the macromolecular substitution reaction, which is one of the important properties of interpolyelectrolyte complexes. In the case of interpolyelectrolyte complexes, the substitution process takes place as a result of the interaction of two complementary macromolecules with subsequent liberation of the third. In the case of polyampholytes, this reaction occurs within the limits of one macromolecule as a result of the formation of a single cooperative system consisting of intrachain ionic and hydrogen bonds and also hydrophobic contacts.

Thus the stability of the polymeric complexes formed from different polyampholyte–polyelectrolyte, polyampholyte–metal ions, and polyampholyte–dye pairs is apparently determined by the competing intramolecular and intermolecular complex formation reactions.

V. Conclusion

On the basis of the detailed study of the mechanism of the binding of metal ions by synthetic polyampholytes, the structures of the complexes, and the regions corresponding to their formation and decomposition, a new procedure has been proposed for the extraction of noble metal ions from dilute solutions.[54] It is based on the "expulsion effect" whose essential feature consists in the ability of synthetic polyampholytes to sorb transition metal ions and to liberate them in the vicinity of the isoelectric point.

A polyampholyte network with a controllable permeability to water and human serum albumin molecules has been synthesised.[53] As can be seen from Fig. 10, the maximum permeation of water molecules through the cross-linked polyampholyte is attained at the isoelectric point. It has been established that the maximum desorption (up to 96%) of the human serum albumin molecules takes place under these conditions. The mechanism of this process apparently consists in the alteration of the pore sizes in the polyampholyte network as a result of the electrostatic interaction of the acidic and basic units, leading to a change in the conformation of the macromolecules.

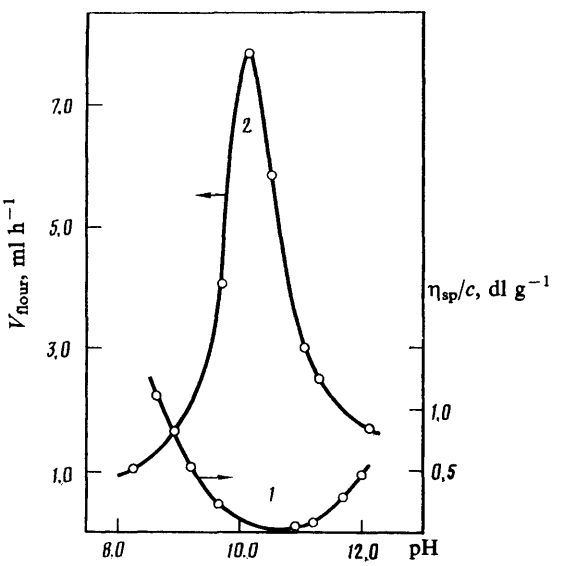


Figure 10. Variation of the intrinsic viscosity (curve *1*) and the permeability to water molecules (curve *2*) for linear (curve *1*) and cross-linked (curve *2*) polyampholytes based on DMVEP-AA with the pH of the solution.[53]

We may point to certain promising ways of using the "expulsion" effect. These are in the first place the creation of a pH-sensitive container which is capable of transporting specific immobilised substances (proteins, enzymes, antibiotics, and medicinal drugs) to the affected regions of the organism and also of "pH-muscles". The idea of creating pH-controlled containers is due to Frenkel'.[81] Let us suppose that a polyampholyte–medicinal drug associated species has been produced. The pH_{IEP} of the polyampholyte is "tuned" to a large section of the given body. So long as the polymeric polyampholyte–drug complex has not reached its "target" the medicinal drug should remain in the bound state. As soon as it reaches the affected region of the organism, whose pH is equal to pH_{IEP}, the drug begins to be released from the bulk of the macromolecular coil of the polyampholyte.

Microscopic conformational transitions are known to lead to macroscopic changes in the dimensions of solid polymers, which permits their use as converters of chemical energy into mechanical energy.[82] Bearing in mind that the polyampholyte–polyelectrolyte polymeric complex is formed cooperatively or decomposes within a very narrow pH range (for example, in the case of the system presented in Fig. 6 the range is 0.1–0.2 pH units), one may expect the creation of pH-muscles or pH-sensors.

We shall consider further the possibilty of creating self-regulating enzyme systems with the aid of polyampholyte–enzyme associated species or conjugates. The main principles governing the creation of a new generation of reversibly soluble immobilised enzymes with the aid of conjugates formed by enzymes with N-PEC have been described in detail.[67,68] On the basis of these principles, one can assume that the active centres of the enzyme bound to the polyampholyte can be "switched off" at the isoelectric point as a result of the formation of dense compact structures and can be "switched on" in the acid or alkaline reigons, i.e. when the chains are uncoiled to the maximum extent. If, for example, the pH of the medium changes as a result of the enzymic reaction, then, after the attainment of pH_{IEP}, the reaction should stop spontaneously.

The idea of using ampholytes with a block structure in matrix synthesis is also attractive. The mechanism of matrix polymerisation on a block polyampholyte chain should not differ fundamentally from the synthesis of polymers on polymeric acid or polymeric base matrices. However, when the reaction is carried out on a block polyampholyte, one may expect the following advantages: (1) the possibility of carrying out matrix polymerisation on individual blocks of the acid or base; (2) an increase in the degree of conversion in the reaction and the formation of water-soluble products maintained in solution and protected against precipitation by the hydrophilic "fringe"; (3) the possibility of separating the polymerisation products from the matrix at the isoelectric point of the block polyampholyte, after which the cyclic process is carried out.

In our view, the above examples and predictions by no means exhaust the theoretical and practical importance of the new property of polyampholytes at the isoelectric point. Further research on these lines is necessary.

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