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Interaction/Formation/Conformation

Interaction of Synthetic Polyampholytes with Anionic and Cationic Detergents in Aqueous Solution

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SUMMARY

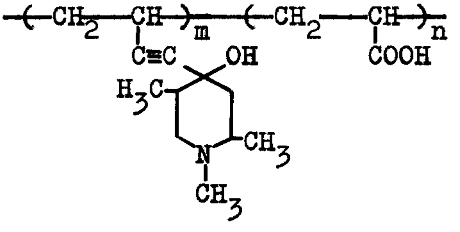
The interaction of amphoteric macromolecules with ionic surfactants is accompanied by a strong decrease of the dimensions of the polyelectrolyte chains, but the complex particles are retained from precipitation by the presence of the hydrophylic components of the polyampholyte. The behaviour of the complex polyampholyte-detergent depends both on the nature of amphoteric copolymers and on the ionic detergents.

INTRODUCTION

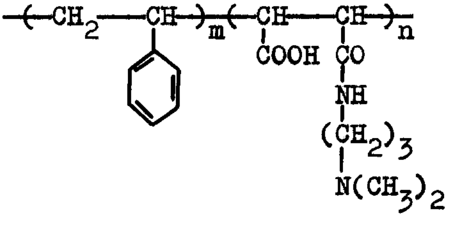
The study of the chemical reaction between synthetic polyelectrolytes and detergents is of great interest (1). Although various extensive investigations have been carried out on the association of polyacids, polybases and nonionic polymers with surfactants, the interaction of amphoteric macromolecules with ionic detergents so far has not been considered.

EXPERIMENTAL

Statistic copolymer of 1,2,5-trimethyl-4-vinylethynil-piperidol-4 and acrylic acid (PA-1) and regular copolymer of styrene and N,N-dimethylaminopropylmonoamide of maleic acid (PA-2) were used:



PA-1



PA-2

$m = 40$ mol.%; $n = 60$ mol.% $\qquad$ $m = n = 50$ mol.%

PA-1 and PA-2 were synthesized by (2) and (3). Potentiometric and conductometric titrations were carried out on the ionomer EV-74 (USSR) and the conductometer OK-102/1 (Hungary) in a thermostat cell at 298±0,1 K. The viscosities of the copolymers and the complexes were measured in water and water-alcohol solutions at 298±0,05 K with a modified

Ubbelohde viscometer described in (4). This procedure simultaneously provided an accurate measurement of the viscosity and the pH of the solutions.

RESULTS AND DISCUSSION

Polyampholytes have an unusual physico-chemical properties due to combination of acid and base groups in polymer chain (5). They are able to interact both with anionic and cationic detergents.

Fig.1 represents the curves of potentiometric and conductometric titrations of polyampholytes with sodium dodecylsulfate (DDS) and cetyltrimethylammonium chloride (CTMA). The observed bends of curves indicate the binding of detergent molecules with copolymers. The composition of the complexes n as determined by the ratio of the active functional group concentrations of PA-1 and PA-2 ($\geqslant$N or $-$COOH) to the detergent is 2:1 mol/mol. It should be noted that the polyampholytes apart from anionic and cationic polyelectrolytes form water-soluble complexes. This feature of complexes polyampholyte-detergent is due to the presence of free noncomplexing hydrophylic components which prevent the complex particles in solution from precipitation.

Viscometric titrations of PA-1 and PA-2 solutions with DDS and CTMA are shown in Fig.2. The addition of anionic surfactant lead to the sharp decrease of relative viscosity of PA-1 in comparison with the cationic one. It may be explained by the difference in degree of binding of surfactant with copolymer. The calculation of the degree of conversion 0 for these systems indicate that the values of 0 are approximately equal to 30% for PA-1/DDS and 5% for PA-2/DDS.

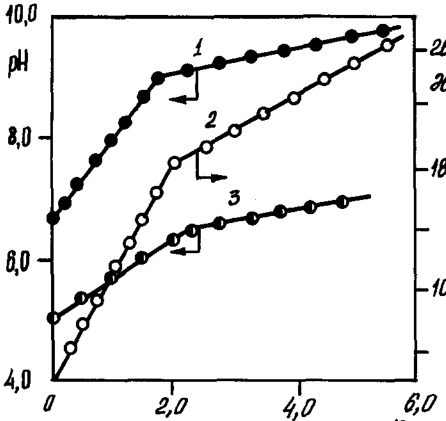


Fig.1. Potentiometric (1,3) and conductometric (2) titration curves of PA-1 with CTMA (2), PA-1 and PA-2 with DDS (1,3) in aqueous solution. [PA-1] = [PA-2] = $1 \cdot 10^{-2}$ mol/l, [DDS] = [CTMA] = $5 \cdot 10^{-3}$ mol/l.

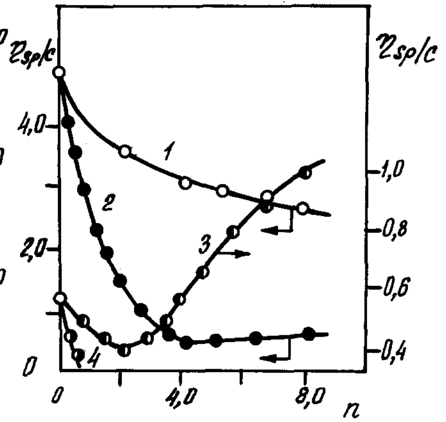


Fig.2. Variation of $\eta_{sp.}/C$ on n for systems PA-1/CTMA (1), PA-1/DDS (2), PA-2/DDS (3), PA-2/CTMA (4). (n is the ratio of detergent concentration to the active functional group concentration of polyampholytes (N or COOH)

It is of interest to consider the influence of copolymer conformation on the complexation reaction. Fig.3 represents the conformational change of PA-1 with the variation of pH solution in the presence and in the absence of surfactant. It is clear that the PA-1 accepts positive and negative charges at pH=4,0 and pH=11,0. In these fields PA-1 has a more expanded conformation. The compact conformation of PA-1 is realized at pH=8,85-8,95, i.e. at the isoelectric point (i.e.p.) of PA-1. Since the binding of detergents and polyelectrolytes is accompanied by the change of pH solution, the interaction of PA-1 and DDS lead to the rise of pH solution and the association of PA-1 with CTMA lead to the reduction of pH solution. From curves 2 and 3 in Fig.3 it follows that the reduced viscosity of the complex PA-1/CTMA decrease when the pH solution increase. At interval of pH = 8,80-11,20 the viscosity of the complex is not dependent on the pH and the complex particles overcoil. Similar effect was established for system PA-1/DDS. In this case the compact conformation is achieved due to the electrostatic interaction between protonated NH^+ ions of PA-1 and SO_3^- anions of DDS. From these results it may be assumed that the sinergetic effect of detergent mixture is stronger than that of individual detergent. Unfortunately this effect can not be examined since the mixture of DDS and CTMA precipitates quickly.

Unlike the PA-1 the PA-2 contain additional styrene groups which will be increase the hydrophobic interaction of unpolar groups of polyampholyte with alkyl chain of detergents. As a result the reduced viscosity of PA-2 sharply decreases with the addition of CTMA solution. Finally the viscosity of PA-2 passes through minimum (Fig.2). The latter may be explained by additional absorption of detergent molecules to the complex particles which lead to the recharge of macromolecules.

Fig.4 represents $\eta_{sp.}/C$ - pH curves for PA-2 and its complex with DDS. At $pH > pH_{i.e.p.}$ the $\eta_{sp.}/C$ of the complex is much higher than that of PA-2. At $pH < pH_{i.e.p.}$ the association of PA-2 with DDS is accompanied by strong compactization of complex particles up to the phase of separation. The above phenomenon becomes clear if we consider the role of the hydrophobic interaction between styrene groups of PA-2 and alkyl chain of DDS leading to the increase of charge density along polymer chain.

The influence of organic solvent on the structure of the complexes PA-1/DDS and PA-1/CTMA is worth mentioning (Fig.5). The variation of viscosity of the complex PA-1/DDS can be divided into three regions, where: 1) the reduced viscosity of the complex is only slightly changed for alcohol contents in the mixture up to 60 vol.%, 2) the reduced viscosity of the complex passes through a maximum at an alcohol content in the mixture of between 60 and 80 vol.%, 3) the reduced viscosity of the complex is only slightly changed when the methanol content in the mixture is higher

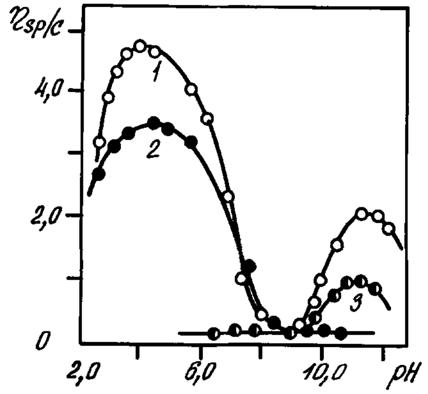


Fig.3. Dependence of reduced viscosity of PA-1 (1) and complexes PA-1/DDS (2), PA-1/CTMA (3) on the pH.

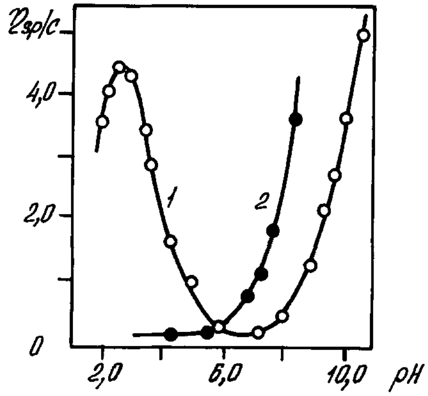


Fig.4. Dependence of reduced viscosity of PA-2 (1) and complex PA-2/DDS (2) on the pH.

than 80 vol.%. These results can be explained as follows: in the first region (1) the compact conformation of the complex is stabilized by hydrophobic interaction. The nonpolar parts of the detergent bound to the polymer chain are oriented inside the coil and lead to the formation of a micellar structure with hydrophobic coils, whereas the hydrophilic (carboxylic) groups of PA-1 are arranged on the surface of the complex particles and are responsible for their solubility; in the second region (2) the complex particles are expanded owing to solvation of the hydrophobic parts of the complex by methanol and hydrophilic ones by water; in the third region (3) the inverse micellar structure is formed. It follows from these considerations that the transition from one compact conformation to another is realized through an extended structure of the complex particles. However, in case of the PA-1/CTMA system η_{sp}/C changed similarly to that of PA-1 itself. This effect can be interpreted by a gradual deterioration of the solvent quality with respect to the hydrophilic parts of the polyampholyte.

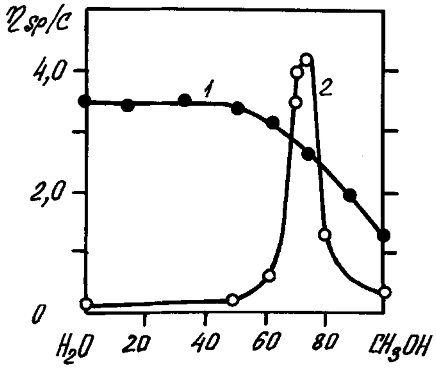


Fig.5. Influence of the solvent composition (in vol.%) of the water-methanol mixture on the reduced viscosity of complexes PA-1/CTMA (1) and PA-1/DDS (2).

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