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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis and Hydrodynamic Behavior of Stoichiometric Complexes of Cationic Polyelectrolytes with Amphiphilic Anions

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Abstract—Complexation of poly(*N*,*N*-dimethyl-*N*-benzyl-*N*-methacryloyloxyethyl)ammonium chloride with oppositely charged amphiphilic compounds was studied. The solubility and hydrodynamic properties of the resulting complexes in chloroform, methanol, and chloroform–hexane and chloroform–toluene mixtures were determined.

Polyelectrolytes (PEs) interact with oppositely charged diphilic ions of micelle-forming surfactants to form polyelectrolyte complexes (PECs) with unique physicochemical properties [1]. Studies of such interactions are necessary for understanding the processes that occur in natural PECs of biopolymers and diphilic compounds [2-4] and the behavior of PECs at flocculation and stabilization of dispersions [5]. It is known [6–9] that stoichiometric PECs (SPECs) formed by anionic surfactants and polydimethyldiallylammonium chloride (PDMDAAC) or poly-N-ethyl-4-vinylpyridinium bromide (PEVPB) (M_w 10⁴-10⁵) are soluble in low-polar organic solvents. However, the features of hydrodynamic behavior of SPECs of macromolecular polyelectrolytes based on aminoalkyl acrylates are still poorly understood. Poly(N,N-dimethyl-N-benzyl-N-methacryloyloxyethyl)ammonium chloride (PE-1) shows promise for preparing hydrophobic complexes, as it has higher molecular weight as compared to poly-N,N-dimethyldiallylammonium chloride (PE-2) and exhibits pronounced hydrophobic properties imparted by the benzyl substituent [10].

In this work we studied the features of interaction between various amphiphilic anions and PE-1 and the hydrodynamic behavior of the resulting SPECs in chloroform, methanol, and mixed solvents.

EXPERIMENTAL

Polyelectrolyte PE-1 was prepared by radical polymerization of the monomer, which was synthesized by alkylation of dimethylaminoethyl methacrylate with benzyl chloride at $0-3^{\circ}$ C in acetone and recrystallized from acetone–acetonitrile mixture. Radical polymerization was performed in an aqueous solution (2 M monomer concentration) at $25\pm0.5^{\circ}$ C up to 96-98% conversion. Then, the polymerizate was dissolved in methanol and precipitated with diethyl ether. *tert*-Butylperoxy-2-propanol used as initiator was prepared by the procedure given in [11]. The resulting polymer was additionally purified by recrystallization from methanol with diethyl ether and dried in a vacuum (1.5–2.0 mm Hg, $20\pm0.5^{\circ}$ C) to constant weight.

In our study we used commercial aqueous solutions of PE-2 (40 wt %). The solutions of PE-2 of various concentrations were prepared from the initial solution by successive dilution.

The intrinsic viscosities of PE-1 and PE-2 determined in 0.1 M NaCl at 30°C were 4.7 and 1.4 dl g^{-1} , respectively.

Anionic surfactants such as sodium dodecyl sulfate SDS (chemically pure grade, Merck) and Volgonatemul'gator (VE) [mixture of sodium salts of alkylsulfonic acids RSO₃Na, $R = C_{16}-C_{18}$, Khimprom Joint-Stock Company, Volgograd, Russia; STP (Enterprise Standard) 2480-282-05763458–99] were used without additional purification.

The stoichiometric polyelectrolyte complexes of surfactants were prepared from the aqueous solutions of components with vigorous stirring. The concentrations of polyelectrolytes and surfactants were 0.01 and 0.1 M, respectively. The resulting precipitate of SPEC was separated, washed with water, and dried in a desiccator to constant weight.

The composition of the reaction mixture Z was determined as the ratio of the concentration of the surfactant ions to the concentration of PE units in the

PE-surfactant	Ζ	SPEC yield, wt %	S, wt %	N, wt %	S/N	φ, mol	η_r , dl g ⁻¹ *
PE-1-SDS	1.0	65	5.5	2.30	2.4	1.00	5.3
	1.5	68	3.1	1.70	1.8	0.80	4.6
	3.0	_	4.7	2.70	1.7	0.76	_
PE-1-VE	1.0	84	5.8	2.28	2.5	1.10	6.3
	1.5	86	4.9	2.56	1.9	0.84	5.2
	3.0	_	5.4	2.20	2.4	1.07	5.1
PE-2–SDS	1.0	59	6.9	2.70	2.5	1.09	_
	1.5	63	_	_	_	_	_
	3.0	_	_	_	_	_	_
PE-2-VE	1.0	38	7.4	3.40	2.2	0.95	_
	1.5	63	_	_	_	_	_
	3.0						

Synthesis of insoluble complexes based on PE-1 and PE-2

* Reduced viscosity of the chloroform solution of the complex (0.2 g dl^{-1}) .

system (Z = [surfactant]/[PE]). The composition of PEC φ was characterized by the ratio of the number of diphilic surfactant ions in PEC to the number of PE units in the polymeric complex ($\varphi = [surfactant]_{PEC}/[PE]_{PEC}$. The composition of the resulting PECs was determined by chemical analysis.

To determine the solubility and hydrodynamic properties of SPECs in organic solvents, the samples were placed in chemically pure grade methanol, chloroform, benzene, toluene, and butyl acetate.

The viscosities of the SPEC solutions in chloroform, methanol, and mixed solvents were measured with an Ubbelohde viscometer (0.34 mm capillary diameter).

A distinctive feature of the interaction of diphilic surfactant ions with oppositely charged macroion is that the phase state of the reaction system depends on the initial reagent ratio Z, and certain Z values characterize different phase states of PECs [12].

In the reaction of PE-1 with SDS and VE, the precipitate is formed only at the reagent ratio close to stoichiometric.

The table shows that quantitative yield of the insoluble complex is never obtained at the stoichiometric reagent ratio, and with increasing Z above the stoichiometric ratio the yield of all the SPECs studied increases. It should be noted that the yields of the complexes in the PE-2–SDS and PE-2–VE systems are lower than those in the corresponding systems with PE-1. The possibility of SPEC formation is determined by the size ratio of the polymer chain and internal surfactant micelles. Moreover, the composition of the precipitated complex can be determined by the polyanion chain length. For example, PEVPB with the degree of polymerization of 1000 yields SPEC with $\varphi = 1.0$ [13], whereas the same polymer with the higher degree of polymerization (2000) gives an insoluble SPEC with $\varphi = 0.85$. A similar trend is observed with the complexes PE-2-SDS and PE-1-VE ($\varphi = 1.09$ and 0.84, respectively). This suggests that certain decrease in φ is associated with the length of the polymeric ion, because the probability of formation of various defects (e.g., loops) increases with increasing length of the polymer chain. These defects are also typical for double-stranded chains of stoichiometric complexes of oppositely charged polymeric ions [14]. These defects are formed owing to conformational noncomplementarity of the polymer chain and surfactant micelles, because the structure of SPEC is a compromise between the conformation of polymeric ion and geometric characteristics of the surfactant aggregates. The mismatch of these parameters will be greater in the case of longer chains, which causes appearance of unlinked sections in the polymer chain. As a result, ϕ of the resulting complexes is smaller than unity.

It is known that the major factor determining whether the polymer will dissolve or swell is its specific interaction with the solvent. In this connection, we studied the behavior of SPECs in various organic solvents. It was found that these complexes dissolve in chloroform and methanol, whereas in aliphatic and aromatic hydrocarbons and ethyl and butyl acetates they occur in the swollen state. Taking into account the polarity and proton-donor power of methanol and chloroform, we suggest that the dissolution of SPECs in them proceeds owing to the solvation of the ion pairs and ester fragments. The other



Fig. 1. Reduced viscosity η_r as a function of PEC concentration *c* in chloroform, methanol, and mixed solvents. (1) Chloroform, (2) methanol, (3) chloroform : hexane = 70 : 30, (4) chloroform : hexane = 50 : 50, (5) chloroform : toluene = 70 : 30, and (6) chloroform : toluene = 50 : 50 (volume ratio in all cases).



Fig. 2. Reduced viscosity η_r of PE-1–VE in the mixed solution as a function of chloroform concentration w_{cl} ; PE-1–VE concentration 0.11 g dl⁻¹. Second component of the solvent: (1) hexane and (2) toluene.

solvents studied cannot dissolve SPECs, as they are incapable of specific interactions with SPECs.

The dependence of the reduced viscosity on the concentration of the complex in methanol is typical for dissociating polyelectrolytes (Fig. 1). The reduced viscosity of the complex η_r in methanol at a concentration *c* 0.015 g dl⁻¹ is 37.1 dl g⁻¹, which is comparable with η_r for PE-1 (43.3 dl g⁻¹). Thus, in methanol the complex dissociates, and owing to the electrostatic repulsion the complex macromolecules occur in the form of a strongly swollen globule.

The solutions of PE-1–VE in chloroform also exhibit abnormal concentration dependences of η_r (Fig. 2), which strongly increases at concentrations

lower that 0.1 g dl⁻¹. Similar effect was observed for complexes of sodium polystyrenesulfonate with alkyltrimethylammonium bromides in ethanol, DMF, and isopropanol [15]. This phenomenon was attributed to the effective charge on the polymer chains even in a low-polarity solvent, which enhances the electrostatic repulsion and increases the hydrodynamic size of the polymer globule. At the same time, in chloroform η_r of the complexes is significantly lower than that in methanol. The η_r values given in the table are comparable with [η] of PE-1 in an aqueous-salt solution (4.7 dl g⁻¹), which suggests that SPECs occur in chloroform as loose swollen globules.

The behavior of the complexes in question strongly differs from that of the complexes based on PDMDAAC or PEVPB for which $[\eta]$ is 0.35– 0.55 dl g⁻¹ and their Huggins constants k' = 0.66 are typical for linear flexible-chain macromolecules in thermodynamically good solvents. The η_r values linearly decrease with dilution, which is typical for uncharged polymers.

Since no dissolution of SPECs in individual hydrocarbons was observed, their hydrodynamic behavior was studied using mixed systems with chloroform and toluene or hexane. The viscometric measurements performed in a wide range of solvent compositions showed no phase separation at a chloroform content from 10 to 90 vol %.

It was expected that addition of hydrocarbons exhibiting affinity for surfactant chains and benzyl groups into the mixed solvent would cause solvation of the above fragments and enhance swelling of the polymer globule. However, as seen from Figs. 1 and 2, in the mixed solvents η_r sharply decreases with increasing hydrocarbon content. This is probably due to the deterioration of the conditions of the ion pair solvation. The effect of this factor is more decisive than the increase of the affinity for the hydrocarbon polymer fragments. As a result, more compact polymer globules are formed in the mixed solvents. Thus, the solubility of the complexes and swelling of their globules are primarily promoted by weakening of the interionic interaction.

The revealed features in the hydrodynamic behavior of PE–surfactant complexes suggest the possibility of their use for modifying the rheological properties of organic liquids.

CONCLUSIONS

(1) Complexing of poly(*N*,*N*-dimethyl-*N*-benzyl-*N*-methacroyloxyethyl)ammonium chloride with anionic surfactants gives hydrophobic complexes (yield 63–86%) with $\varphi = 0.8-1.1$ at the initial component ratio Z = 1-3.

(2) Solutions of the polymeric complexes in methanol and chloroform exhibit abnormal hydrodynamic behavior typical for polyelectrolytes. The solubility and high viscosity of solutions of the complexes are enhanced by solvation of the ion pair and polar fragments with proton-donor solvents.

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