Structure and Properties of Polyelectrolyte−Surfactant Nonstoichiometric Complexes in Low-Polarity Solvents

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ABSTRACT: Solutions of complexes of poly(*N*-ethyl-4-vinylpyridinium) cations and dodecyl sulfate anions in chloroform are studied by viscometry, isothermal diffusion, flow birefringence, and dynamic light scattering techniques. Stoichiometric polyelectrolyte−surfactant complexes as well as nonstoichiometric ones with the compositions 0.55−1.0, expressed as the molar ratio of surfactant ions to the polycation chain units, neither form interchain associations nor dissociate into individual components in dilute solutions in chloroform. A decrease in the complexes' composition, i.e., a substitution of dodecyl anions with bromide anions, results in an increase of diffusion coefficients and a decrease in the intrinsic viscosity and in the absolute value of the negative segmental optical anisotropy of macromolecules of such complexes. Solubility of the studied complexes in low-polarity solvents increases in the order chloroform > chlorobenzene > benzene and decreases with decrease in the composition of complexes. Interchain associations dominate in dilute solutions of the complexes in chlorobenzene. Introduction of 1 vol % of cosolvent (methanol) to the dilute solutions of the complexes in chloroform and chlorobenzene (i) does not cause any change in the diffusion coefficient of the stoichiometric complex in chloroform, (ii) causes a decrease in the diffusion coefficient of the nonstoichiometric complexes in chloroform down to the value close to that of the stoichiometric complex, and (iii) causes an increase (more than an order of magnitude) in the diffusion coefficients of stoichiometric and nonstoichiometric complexes in chlorobenzene up to the values close to those of complexes in chloroform.

Introduction

Complexes based on polyelectrolytes and oppositely charged surfactants (PEC) are formed in aqueous solutions due to Coulombic attraction between polyion chain units and surfactant ions, and they are stabilized by hydrophobic interactions of nonpolar fragments of surfactant. At present, the regularities of formation and structure of such complexes in aqueous solutions have been studied in detail.[1−10] Depending on the polyelectrolyte to surfactant ratio, the formation of stoichiometric or equimolar complexes (SPC) and nonstoichiometric complexes (NPC) may occur. In the latter case, the composition of the complexes formed (φ), expressed as the molar ratio of surfactant to polycation chain units, normally does not exceed 0.3−0.5. An increase of surfactant concentration in the mixture above 0.3−0.5 results in a disproportionation reaction.[7,8] As a result of disproportionation, phase separation occurs. The precipitate consists of SPC, while NPC of the same φ remains in solution. Further increase in surfactant concentration leads to an increase in the mass of the precipitate, SPC, while still no change in the NPC composition is observed. Thus, a disproportionation reaction in polyelectrolyte−surfactant aqueous solutions driven by hydrophobic interactions precludes synthesis of NPC with $\varphi > 0.3-0.5$ via direct mixing of oppositely charged components.

At the present time, there is a lack of information on the behavior of PECs in nonaqueous and specifically low-polarity organic solvents. Some recent studies of PEC behavior in alcohol−water mixtures indicate dissociation of PECs.[11,12] One can expect that the amphiphilic structure of PECs will promote solubility of such complexes in low-polarity organic solvents. We have found recently that SPCs based on various synthetic linear polyelectrolytes and surfactants are soluble in some low-polarity organic solvents such as chloroform, benzene, etc.[13] This has allowed us to use mixed organic solvents to synthesize NPCs based on polyelectrolytes and oppositely charged surfactants, containing relatively small amounts of polyelectrolyte chain units ($\varphi = 0.95-0.70$), in which surfactant counterions are substituted for simple low-mass counterions.[14] Preliminary data on the behavior of SPCs and NPCs in chloroform obtained by velocity sedimentation and viscometry suggest a similarity in the behavior of NPCs and ionomers.[14]

Further studies of the structure and properties of SPC and NPCs in low-polarity organic solvents using viscometry, flow birefringence, isothermal diffusion, and dynamic light scattering techniques have been undertaken in this work using poly(*N*-ethyl-4-vinylpyridinium) bromide and sodium dodecyl sulfate as initial

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Scheme 1

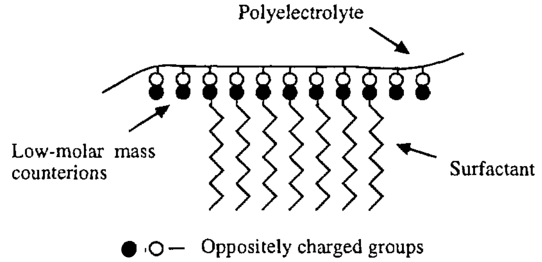

Table 1. Compositions of the Nonstoichiometric Complexes

abbreviation	$\varphi = n/(n + m)$	abbreviation	$\varphi = n/(n + m)$
SPC	~1.0	NPC_3	0.70
NPC_1	0.95	NPC_4	0.55
NPC_2	0.85		

components. Solubilities of NPCs and SPC are studied in chloroform, chlorobenzene, and benzene. The conformational state and aggregation behavior of NPCs and SPC are studied in some of the above-mentioned solvents and also in the presence of 1 vol % of cosolvent methanol.

Experimental Section

Materials. Poly(*N*-ethyl-4-vinylpyridinium) bromide (PEVP) was synthesized by quaternization of poly(4-vinylpyridine) as described elsewhere.[13,14] The degree of quaternization was 93 ± 2.5% as established by IR and UV spectroscopy.[13] Poly(4-vinylpyridine) (P4VP) with viscosity-average molar mass M_η = 300 000 (Scientific Polymer Products) and sodium dodecyl sulfate (SDS) purchased from Sigma (99% purity) were used as received. SPC was obtained via mixing aqueous solutions of PEVP and SDS. The precipitate, i.e., SPC, was isolated, washed twice with distilled deionized water and dried over P_2O_5 in a vacuum desiccator for 5 days.[13,14] The composition of the SPC was estimated using elemental analysis and UV spectroscopy. Good correlation was observed between experimental and calculated values of C, N, and H contents corresponding to the equimolar ratio of the components in the PEVP–SDS complex: $C_{exp} = 60.5\%$, $H_{exp} = 9.4\%$, $N_{exp} = 3.45\%$; $C_{cal} = 63\%$, $H_{cal} = 9.3\%$, $N_{cal} = 3.5\%$. The content of polycation was also estimated by UV spectroscopy (the absorption band of the pyridinium chain units in chloroform–methanol mixture is located around $\lambda = 257$ nm), while the amount of surfactant was calculated from the known total weight of the sample and the estimated polycation content. It was found that 98 ± 3.0% of the polycation chain units were carrying dodecyl sulfate counterions. NPCs were synthesized via an ion-exchange reaction between SPC and PEVP mixed at the proper ratio φ in chloroform (99.5 vol %)–methanol (0.5 vol %) solvent as was described previously.[14] The NPCs thus obtained with various compositions $\varphi = n/(n + m)$, where n and m are the molar contents of polycation chain units with dodecyl sulfate and bromide counterions, respectively, were used in our studies (see Table 1 and Scheme 1). Chloroform, chlorobenzene, and benzene were thoroughly purified from trace amounts of water and alcohol as described in our previous publication.[13]

Preparation of Solutions. Solutions of polyelectrolyte–surfactant complexes in low-polarity solvents were prepared volumetrically by dissolution of the initial samples using magnetic stirrers for agitation for about 24 h and with the subsequent dilution of the solutions thus obtained.

Measurements. Flow birefringence (FB) studies were performed using a dynamo-optimeter setup with inner rotor and photoelectric registration.[15] The height of the rotor in the direction of the light beam was 34 mm, and the width of the rotor-to-stator gap was 0.3 mm. FB was measured using a compensating device with modulation of elliptical light polarization and a He–Ne laser as the light source. The compensator (thin mica plate) produced a phase difference corresponding to 0.36 wavelength (632.8 nm). The FB experimental setup is described in more detail elsewhere.[15]

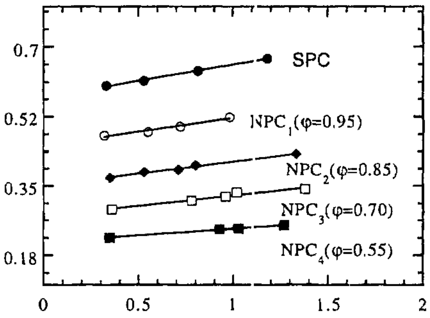

Figure 1. Reduced viscosity of SPC and NPCs of various compositions, φ, versus concentration in chloroform.

Table 2. Hydrodynamic and Conformational Characteristics of SPC and NPCs of Various Compositions in Chloroform

complex	φ	⟨DP⟩ × 10^{-3}	[η], dL/g	k	$D \times 10^7$, $cm^2 \cdot s^{-1}$	$M_{D\eta}$ × 10^{-6}	M × 10^{-6}	A, nm
SPC	1.0	3.0	0.57	0.25	1.88	1.4 ± 0.3	1.2	5.2
NPC_1	0.95	3.0	0.46	0.31	2.06	1.4 ± 0.3	1.2	4.9
NPC_2	0.85	3.0	0.35	0.49	2.21	1.4 ± 0.3	1.1	4.3
NPC_3	0.70	3.0	0.28	0.52			1.0	3.6
NPC_4	0.55	3.0	0.21	0.61	2.78	1.2 ± 0.27	0.93	2.7

Isothermal diffusion experiments were carried out in a double-sector cell with optical length of 20 mm and temperature kept constant at 298 K (±0.005 K). The first sector was used for a solvent and second for a solution. The sectors were connected via a thin capillary. A boundary between solvent and solution was formed by artificial layering of a solvent onto the solution. The concentration gradient for a diffusion process, dc/dx, is equal to (dn/dx)(∂c/dn), where dn/dc is the increment of solution refractive index. The time dependence of a diffusional boundary profile was followed using a Lebedev polarization interferometer. Beam splitting by a spar was equal to 1 mm.[15,16]

Dynamic light scattering studies were carried out using a Coherent Innova Series Ar ion laser operated at wavelength $\lambda = 514.5$ nm and an ALV 5000 multichannel digital correlator. The obtained experimental autocorrelation functions were analyzed using the CONTIN program as described in our previous publication.[17] All measurements were carried out at 293 K.

Viscosity measurements were performed using an Ostwald-type capillary viscometer. The flow time for chloroform was 81.4 s. The temperature was kept constant at 293 K.

Refractive index measurements were carried out using an IRF-23 refractometer operated at the wavelength $\lambda = 546.0$ nm, corresponding to the mercury green band. The temperature was kept constant at 293 K.

Results and Discussion

As has been shown earlier in our publication,[14] SPC based on poly(*N*-ethyl-4-vinylpyridinium) cations and dodecyl sulfate anions as well as NPCs, in which the dodecyl sulfate anions are partially substituted for bromide anions, are soluble in chloroform. We have studied complexes of the above-mentioned type with compositions $\varphi = 0.55–1.0$.

Figure 1 shows the dependencies of the reduced viscosities of SPC and NPCs with various compositions on the concentration of the complexes in chloroform. These dependencies can be approximated by straight lines. An extrapolation to zero concentration was used to obtain the values of the intrinsic viscosities, while the values of the Huggins constants were estimated from the slopes. The data are summarized in Table 2

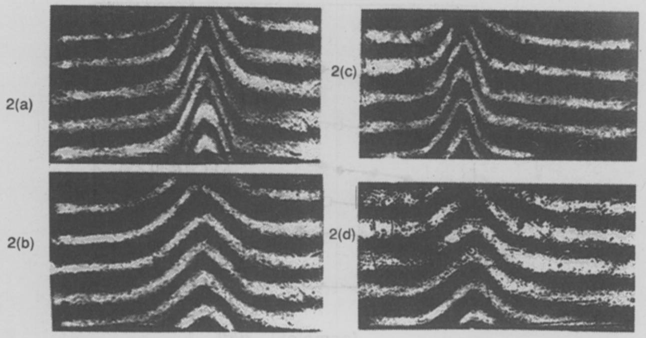

Figure 2. Interferential curves obtained for the diffusion of the nonstoichiometric complexes in chloroform at different moments of time after the beginning of the experiment: NPC$_2$-(φ=0.85), c = 0.217 g/dL, t = 3 h (a) and t = 8 h (b); NPC$_1$-(φ=0.95), c = 0.215 g/dL, t = 4.5 h (c) and t = 8 h (d).

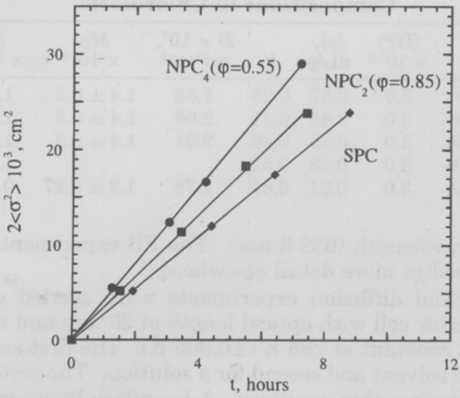

Figure 3. Dispersion of the diffusion pattern versus time for the complexes of various compositions in chloroform: SPC, c = 0.215 g/dL; NPC$_2$(φ=0.85), c = 0.217 g/dL; NPC$_4$(φ=0.55), c = 0.245 g/dL.

for the complexes with φ = 0.55−1.0. The Huggins constant (k) ranges from 0.25 to 0.61, which is characteristic of flexible-chain polymers. A decrease in φ causes an increase in the Huggins constant, which indicates a change from thermodynamically "good" solvent for SPC and NPC(φ=0.95) to "poor" solvent for NPC(φ=0.55). The intrinsic viscosity decreases with decrease in composition of the complexes and approaches values for flexible-chain polymers with the same degree of polymerization.

We have estimated diffusion coefficients of SPC and NPCs in the dilute solutions in chloroform using the isothermal diffusion technique. Figure 2 shows photographs of the diffusion border profiles of NPCs at different times. The data in Figure 2 were used to calculate the dispersion of the diffusion border profiles ($\langle\sigma^2\rangle$) using the method of square and maximum ordinate and assuming a Gaussian form of the diffusion pattern.[15] Figure 3 shows the dependencies of $\langle\sigma^2\rangle$ on time for the complexes of various compositions. The dependencies of $\langle\sigma^2\rangle$ versus time are well approximated by straight lines, the slopes of which give the average values of the diffusion coefficients; see Table 2. As one can see in Table 2, the diffusion coefficient (D) increases with decrease in φ, thus indicating contraction of NPC coils in the dilute solution in chloroform.

In order to study possible aggregation in the solutions of the complexes, we have used the dynamic light scattering technique. Table 3 shows concentration dependencies of diffusion coefficients (D_m) for the complexes of various compositions as well as for poly(4-vinylpyridine)—a precursor for the synthesis of PEVP—in dilute solutions in chloroform. Very small concentration deviations in the diffusion coefficients are observed for nearly all the samples, thus indicating no interchain aggregation in the concentration intervals studied for the complexes and the polymer precursor. The values of D_m of the complexes and the polymer precursor are in order of magnitude agreement with those values characteristic of individual coils. The presence of a "slow" diffusion component at the highest concentration of NPC(φ=0.55) cannot be directly related to the presence of interchain associations in NPC(φ=0.55) solutions, since the analogous component also appears in the case of the polymer precursor. Note that the obtained D_m values correspond to the translational diffusion of macromolecular coils themselves, since we have not observed any angular dependence of D_m in the interval 25−90° for the whole studied range of polymer/complex concentrations. The values of the diffusion coefficients obtained by extrapolation of D_m concentration dependencies to zero concentrations for all complexes and the polymer precursor are also given in Table 3. Good correlation is observed between diffusion coefficients obtained by dynamic light scattering and isothermal diffusion techniques (Tables 2 and 3).

Table 3. Diffusion Coefficients of Polymer Precursor and Complexes of Various Compositions in Chloroform, Estimated from DLS Data Using CONTIN Analysis

concn, g·dL^{-1}	$D_z \times 10^7$, cm^2·s^{-1}					
	P4VP	SPC	NPC$_1$	NPC$_2$	NPC$_3$	NPC$_4$
0.13	2.49	1.83	2.06	2.13	2.40	2.96
0.20	2.51	1.85	2.09	2.13	2.45	2.89
0.32	2.47	1.96	2.04	2.19	2.28	2.81
0.64	2.36	1.89	2.00	2.26	2.30	2.77
1.29	2.45; 0.11	2.13	2.11	2.40	2.34	2.92; 0.26
$C \to 0$	2.50	1.82	2.05	2.10	2.41	2.87

We have estimated molar masses ($M_{D\eta}$) of the complexes using experimental data for D, [η], and the known value of the hydrodynamic invariant $A_0 = (3.2 \pm 0.2) \times 10^{-10}$ erg/K·mol$^{-1/3}$ by the following well-known relationship:[15]

$$M_{D\eta} = (A_0 \mathrm{T} D/\eta_0)^3 \times 100/[\eta] \qquad (1)$$

An estimated $M_{D\eta}$ values correlate within the experimental error with molar masses (M) calculated from the known polymerization degree of PEVP (Z) and compositions of the complexes:

$$M = Z[\varphi M_1 + (1 - \varphi)M_2] \qquad (2)$$

where M_1 and M_2 are the molar masses of polycation chain units with either dodecyl sulfate anions or bromide anions as counterions (Table 2).

Linear dependence of intrinsic viscosity on concentration, preservation of symmetrical diffusion pattern in time, weak dependence of D_m on concentration of the complexes, and good correlation between $M_{D\eta}$ and M values indicate that synthesized SPC and NPCs are individual compounds undergoing neither aggregation nor dissociation into initial components in the dilute solutions in chloroform.

We have used the Flory equation to estimate Kuhn segment lengths (A) for NPC$_2$(φ=0.85) and NPC$_3$-(φ=0.70) for which the values of the Huggins constant are close to 0.5, thus corresponding to "Θ conditions":

$$[\eta] = \Phi\langle h^2\rangle^{3/2} M = \Phi A^{3/2}(\lambda Z)^{1/2}/M_0 \qquad (3)$$

where $\Phi = 2.1 \times 10^{21}$ mol^{-1} is the Flory constant, λ =

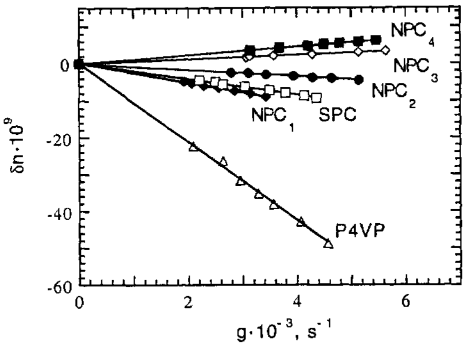

Figure 4. Flow birefringence versus gradient of flow velocity for the polymer precursor and the complexes of various compositions in chloroform: SPC, c = 0.812 g/dL; NPC$_1$(φ=0.95), c = 0.98 g/dL; NPC$_2$(φ=0.85), c = 1.335 g/dL; NPC$_3$(φ=0.70), c = 1.02 g/dL; NPC$_4$(φ=0.55), c = 0.918 g/dL; P4VP, c = 1.554 g/dL.

0.25 nm is the projection of the monomer unit on the chain direction, and $M_0 = M/(Z\lambda)$ is the molar mass of the chain unit length, calculated using the known chemical structure and composition of the complexes; see eq 2. The values of A (Table 2) are within the same order of magnitude as those of flexible-chain polymers and comblike copolymers with side chain groups of the same length of the hydrocarbon fragments of the surfactant counterions in our case.[15]

In order to estimate Kuhn segment lengths of SPC, NPC$_1$(φ=0.95), and NPC$_4$(φ=0.55) for which the values of the Huggins constants substantially differ from 0.5, we have used the flow birefringence (FB) technique. Figure 4 shows the dependencies of FB values (δn) upon the gradient of flow velocity for the SPC, NPCs, and polymer precursor solutions. All dependencies are well approximated with straight lines, passing through the coordinates' zero point. The values of the optical shear coefficients ($\delta n/\delta\tau$, $\delta\tau = g(\eta - \eta_0)$ is the shear stress caused by macromolecules in laminar flow in solution) calculated from the slopes of the straight lines are given in Table 4. The $\delta n/\delta\tau$ value strongly depends on the composition of the complexes. The sign of $\delta n/\delta\tau$ changes from negative to positive while passing from NPC$_3$(φ=0.70) to NPC$_4$(φ=0.55). As is shown, $\delta n/\delta\tau$ in polymer solutions depends on the optical anisotropy of the chain units, the equilibrium rigidity of the macromolecules, and the effects of "microform" and "macroform".[15] An additional dependence of $\delta n/\delta\tau$ on form effects appears when the refractive indexes of solvent (n_0) and solution (n) do not coincide, as in our case. Thus, the $\delta n/\delta\tau$ value can be expressed as the sum of the self optical anisotropy of macromolecules (θ_i), which depends on the chemical structure of the polymer chain unit and the Kuhn segment length, form asymmetry of the macromolecular segment (θ_{fs}) ("microform"), and form asymmetry of the macromolecular coil (θ_f) ("macroform"):[15]

$$\delta n/\delta\tau = [4\pi({n_0}^2 + 2)^2][\theta_i + \theta_{ds} + (9.4)\theta_f]/27kTn_0 \quad (4)$$

where $\theta_i = 3\delta\alpha_l/5$ (for flexible-chain macromolecules with the assumption of Gaussian coil conformation),[15] $\theta_{fs} = (3/5)[(\mathrm{d}n/\mathrm{d}c)]^2[(M_0{}^2[\eta]^{2/3})/(N_a\pi\rho\Phi^{2/3}M^{1/3})]e_s$, $\theta_f = 8.33[(\mathrm{d}n/\mathrm{d}c)/(2\pi N_a\rho)]^2(M\Phi)/[\eta]$ according to refs 15 and 17, n_0 is solvent refractive index, k is the Boltzmann constant, N_a is Avogadro's number, ρ is polymer density, $\delta\alpha_l$ is the optical anisotropy of the Kuhn segment length, and e_s is the form coefficient of a polymer segment, taken as for comblike copolymers with the side chain groups of the same length as the length of the surfactant hydrocarbon radicals in our case.[18] The values $\delta\alpha_l$ for the studied complexes and the polymer precursor (Table 4) were calculated using eq 4 and experimental values: $\delta n/\delta\tau$, dn/dc, n_0, M, [η], ρ = 1.1 g/cm^3, e_s = 0.3.

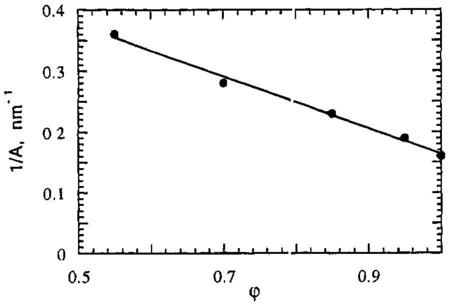

Figure 5. Inverse Kuhn segment versus composition of the complexes. Solvent: chloroform.

Table 4. Dynamo-optical Characteristics of the Complexes in Chloroform

complex (polymer)	φ	dn/dc, cm^3/g	$\delta n/\delta\tau \times 10^{10}$, cm·s/g	$\delta\alpha_l \times 10^{25}$, cm^3	$\beta \times 10^{17}$, cm^2
SPC	1.0	0.055	−12.0	−320	−6.2
NPC$_1$	0.95	0.056	−9.0	−290	−6.0
NPC$_2$	0.85	0.059	−3.0	−240	−5.6
NPC$_3$	0.70	0.056	−2.5	−180	−5.0
NPC$_4$	0.55	0.054	8.0	−120	−4.4
P4VP		0.097	−9.0	−220	−

All complexes have negative $\delta\alpha_l$ values analogous to vinyl and acrylic type polymers carrying anisotropic side chain groups with the axes of maximum optical polarization oriented perpendicular to the main chain.[15] One can estimate the values of the self optical anisotropy of the chain unit length as $\beta = \delta\alpha_l/A$ for NPC$_2$(φ=0.85) and NPC$_3$(φ=0.70) (Table 4). One can assume that the following relationship is valid for all the complexes:

$$\beta = \beta_1(1 - \varphi) + \beta_2\varphi \quad (5)$$

where β_1 and β_2 are the values of the optical anisotropy of the chain unit length for the polycation chain units carrying either dodecyl sulfate or bromide counterions, respectively. The values of β_1 and β_2 calculated using eq 5 for NPC$_2$(φ=0.85) and NPC$_3$(φ=0.70) are equal to 6.2 × 10^{-17} and 2.3 × 10^{-17} cm^2, respectively. The β_1 and β_2 values obtained are within an order of magnitude of those characteristic of vinyl and acrylic type polymers with anisotropic side groups of various lengths.[15] The values of β for other complexes were calculated using eq 5 and known β_1 and β_2 values (Table 4). The value of β undergoes similar changes with the decrease in φ as for the case of $\delta\alpha_l$. Finally, we have estimated Kuhn segment lengths for the rest of the complexes, $A = \delta\alpha_l/\beta$, (Table 2).

One can suggest that the decrease in intrinsic viscosities, increase in diffusion coefficients, and decrease in absolute values of $\delta\alpha_l$ with a decrease in φ are related to the contraction of the macromolecular coils in chloroform.

Note that the Kuhn segment length decreases nearly twice its value while passing from SPC to NPC$_4$(φ=0.55) (Table 2). A linear dependence of flexibility (1/A) of macromolecular coils on the composition of the complexes is observed for SPC and the NPCs (Figure 5). One can assume that coil contraction is related to a decrease in the rigidity of the macromolecules as the result of substitution of bulky dodecyl sulfate anions for bromide

Table 5. Solubility of (PEVP−SDS) Complexes of Various Compositions in Low-Polarity Solvents

solvent	φ = [SDS]/[PEVP], (mol/base-mol)	solubility of complexes
chloroform	1.0−0.50	soluble at room temp
chloroform	≤0.45	not soluble at all T
chlorobenzene	1.0−0.85	soluble at room temp
chlorobenzene	<0.85−0.75	not soluble at all T
benzene	0.95	soluble at $T \geq$ 40−45 °C
benzene	0.90−0.85	soluble at $T \geq$ 70−75 °C
benzene	≤0.45	not soluble at all T

anions in the complex particles. Also, the observed contraction may be caused by the "ionomer" nature of the NPCs, i.e., aggregation of more polar polycation chain units carrying bromide counterions in low-polarity chloroform solvent. We have estimated the root mean square end-to-end distance, $\langle h^2\rangle^{1/2}$, for SPC and NPC_1(φ=0.95) coils in chloroform and also at "Θ-conditions", $\langle h_0^2\rangle^{1/2}$. The values of $\langle h_0^2\rangle^{1/2}$ can be calculated using the relationship for a Gaussian chain:

$$\langle h_0^2\rangle^{1/2} = (AM/M_0)^{1/2} \qquad (6)$$

and the values of $\langle h^2\rangle^{1/2}$ can be calculated using eq 3. The ratio of those values, $\langle h^2\rangle^{1/2}/\langle h_0^2\rangle^{1/2}$, is equal to 1.11 and 1.05 for SPC and NPC_1(φ=0.95), respectively. Such a decrease in $\langle h^2\rangle^{1/2}/\langle h_0^2\rangle^{1/2}$ ratio while passing from SPC to NPC_1(φ=0.95) can be related to the "poorer" hydrodynamic quality of the solvent in the latter case and, therefore, to the contraction of NPC_1(φ=0.95) coils as the result of substitution of hydrophobic surfactant counterions for polar bromide anions in the complex particles. In order to reveal the "ionomer" nature of NPCs, we have studied the solubility of SPC and the NPCs in various low-polarity solvents and have investigated the influence of methanol cosolvent for ionomer polar groups[19] on the behavior of SPC and NPCs in chloroform and chlorobenzene using the dynamic light scattering technique.

The results of the studies of the solubility of SPC and NPCs in low-polarity solvents are given in Table 5. One can dissolve SPC and NPCs containing up to 50 molar % of polycation chain units with bromide counterions. The composition of the complexes soluble in chlorobenzene is limited to 15−25 molar % of the same chain units. Solubility of such complexes in benzene is lower, the composition of soluble complexes does not exceed φ = 0.85, and the solubility of the complexes depends on temperature (see Table 5).

Thus, the solubility of NPCs depends on the nature of the low-polarity solvent and decreases in the order chloroform > chlorobenzene > benzene, which correlates with a decrease in the solvation tendency of NPC salt groups and with a decrease in donor-acceptor properties of the above-mentioned solvents in the same sequence.[20] A decrease in solubility of the complexes, i.e., an enhancement of aggregation of polycation polar chain units in NPCs in the above-considered order of solvents, confirms the "ionomer" nature of NPCs.

It is known that the introduction of a small amount of alcohol (about 1 vol %) to the ionomer solution in such low-polarity solvents as *m*-xylene leads to a substantial increase in the ionomer solubility and is accompanied by a sharp decrease in the viscosity of semidilute ionomer solutions.[19] It was suggested that the low molar mass additive (methanol) efficiently solvates the ionomer salt groups, which leads to the disruption of associations of the salt groups and thus causes an increase in ionomer solubility in *m*-xylene. One can anticipate analogous effects for the NPCs.

Table 6. Diffusion Coefficients of the Complexes of Various Compositions in Chloroform−Methanol Mixtures, Estimated from DLS Data Using CONTIN Analysis

complex	solvent	concn, g/dL	$D_z \times 10^7$, $cm^2 \cdot s^{-1}$
SPC	CH_3Cl (99 vol %)+ CH_3OH (1 vol %)	$C \rightarrow 0$	1.84
NPC(φ=0.70)	CH_3Cl (99 vol %)+ CH_3OH (1 vol %)	$C \rightarrow 0$	1.94

Table 7. Diffusion Coefficients of the Complexes of Various Compositions in Chlorobenzene and Chlorobenzene−Methanol Mixtures, Estimated from DLS Data Using CONTIN Analysis

complex	solvent	concn, g/dL	$D_z \times 10^7$, $cm^2 \cdot s^{-1}$
SPC	C_6H_5Cl	0.026	0.19
SPC	C_5H_5Cl (99 vol %)+ CH_3OH (1 vol %)	0.13	1.64
NPC(φ=0.95)	C_6H_5Cl (99 vol %)+ CH_3OH (1 vol %)	0.13	1.98
NPC(φ=0.85)	C_6H_5Cl (99 vol %)+ CH_3OH (1 vol %)	0.13	1.88; 0.25

The data on the influence of methanol (1 vol %) on the zero-concentration diffusion coefficients of SPC and NPC_3(φ=0.70) in chloroform−methanol solvent are shown in Table 6. The presence of small amounts of cosolvent methanol does not influence the D values of the SPC and leads to a decrease in D of the NPCs down to the value close to that of D(SPC). A decrease in D of the NPC can be related to the "unfastening" and expansion of polymer coils due to the disruption of intrachain associations of polar chain units of the NPC, which causes contraction of the NPC coils in the absence of methanol. Such a behavior is characteristic of ionomers.

The results of the study of the complexes in chlorobenzene also support the "ionomer" nature of the NPCs (Table 7). Dominating interchain aggregation is observed in dilute solutions of SPC and the NPCs in chlorobenzene. Dissolution of the SPC solution down to 0.026 g/dL, corresponding to the sensitivity limit of the dynamic light scattering technique, allows one to measure the diffusion coefficient of SPC, which is still an order of magnitude lower than the diffusion coefficients of SPC and the NPC individual coils. In the case of NPCs (φ = 0.95, 0.85) at the same concentrations, the average size of the aggregates is larger than the average pore diameter of the filter (0.5 μm). Introduction of 1 vol % of methanol into the SPC and NPC solutions in chlorobenzene leads to a sharp increase in the diffusion coefficients up to the values characteristic of individual coils. A slight difference in the behavior of SPC and NPCs is still observed. The diffusion coefficient of SPC is smaller than that of NPC, and in the case of NPC(φ=0.85) with the higher content of polar chain units one can observe a "fast" component, corresponding to diffusion of individual coils, as well as a "slow" component ascribed to diffusion of macromolecular aggregates. One can conclude that addition of alcohol leads to efficient disruption of interchain aggregates of salt groups in the complexes, which dominate in the SPC and NPC solutions in chlorobenzene. The observed differences in the character of salt group aggregation in the SPC and the NPCs in chlorobenzene both in the presence and in the absence of methanol confirm the "ionomer" nature of the NPCs.

The above-considered NPCs possess some specific features. One of them is that aggregation of the "salt groups" in NPC "ionomers" can be accompanied by migration of salt groups due to ion-exchange reactions in the NPC particles. The possibility of such migration may be supported by the reaction of NPC formation carried out via ion-exchange between SPC and free polyion in the mixed low-polarity organic solvents.[14] As the result of such migration, in contrast to traditional ionomers, one can expect formation of ordered, nonstrained networks in the NPC "ionomers" and possible segregation of polar chain units in the NPCs with the formation of amphiphilic structures similar to block copolymers.

The other specific feature of such amphiphilic complexes is that due to the presence of surfactant counterions the conformational state of NPC and SPC, as follows from our studies, is similar to that of comblike polymers. Thus, one can anticipate that such complexes will behave as self-organized systems capable of forming various types of mesomorphic structures due to interactions of side chain groups, the hydrocarbon fragments of the surfactant molecules. The results of our preliminary studies, carried out using DSC, X-ray analysis, and polarizing microscopy, have shown that NPCs and SPC in the condensed phase do form mesomorphic structures which are like those of comblike polymers with backbone and side groups of similar nature.[21] Similar results indicating the formation of mesomorphic structures for stoichiometric polyelectrolyte–surfactant complexes have been obtained earlier on the example of common synthetic polyelectrolytes by Antonietti et al.,[22] as well as with poly(glutamic acid) in an ionized form in our recent publication.[23] Our DSC experiments carried out for poly(*N*-ethyl-4-vinylpyridinium) cation–cetyl sulfate anion complexes of various compositions have shown a decrease in melting temperatures of mesophases with a decrease in φ, while the melting enthalpy of the complexes estimated per mass of the structural segment of NPC complex containing only surfactant counterions was nearly constant, thus confirming migration and segregation of polar chain units in the NPCs.[21] Therefore, one can anticipate that such amphiphilic supramolecular structures which are capable of self organization will be the subject of investigations in the near future.

Concluding Remarks

The experimental data lead to the conclusion that SPC, composed of a polyelectrolyte and oppositely charged surfactants, and the new NPCs represent amphiphilic compounds soluble in some low-polarity organic solvents with the formation of molecular solutions. The NPCs represent a novel type of ionomer in which excessive polyion chain units carrying simple low-mass counterions play the role of the ionomer "salt groups" capable of aggregating in low-polarity solvents, while the hydrophobic structural segments of the NPCs composed of polyion chain units and surfactant counterions provide the solubility of the NPCs in low-polarity organic solvents. The aggregation of excessive polyelectrolyte chain units in NPC-based ionomers may be accompanied by segregation of the NPC ionomer "salt groups" due to proceeding of ion-exchange reaction in NPC particles in low-polarity chloroform solvent. Further investigation of the behavior of such complexes using dynamic and static studies of electric birefringence of SPC and NPCs may be useful to reveal segregation in nonstoichiometric complexes.

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