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Poly(*N*-ethyl-4-vinylpyridinium bromide)–sodium dodecyl sulfate complexes. Formation and supramolecular organization in salt containing aqueous solutions

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Abstract

Formation and supramolecular organization of poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVP)–sodium dodecyl sulfate (SDS) complexes in aqueous-salt solutions have been studied. PEVP samples of three polymerization degrees ($P_w = 570$, 1200 and 2350) were used. For PEVP of lower polymerization degree ($P_w = 570$) only insoluble complexes were observed in the whole range of the reaction mixture composition studied: $Z = [\mathrm{SDS}]/[\mathrm{PEVP}] \leq 1$. For PEVP of higher polymerization degrees ($P_w = 1200$ and 2350), water-soluble complexes are formed up to a critical value of the reaction mixture composition, Z, that is similar for both PEVP fractions. It was found that water-soluble complex species are either molecularly dispersed (i.e. each complex particle comprises only one macromolecule) or aggregated (includes about 40 polymer chains and 20,000 surfactant ions) depending on the complex composition. Complex composition, in its turn, was shown to be determined by PEVP polymerization degree and the reaction mixture composition.

Keywords: Polyelectrolyte–surfactant complex; Supramolecular organization; Poly(*N*-ethyl-4-vinylpyridinium)

1. Introduction

Interaction of polyelectrolytes (PE) with oppositely charged micelle-forming surfactants (S) results in the formation of polyelectrolyte–surfactant complexes (PSC) [1,2]. Two main driving forces are known to introduce into such interaction: electrostatic attraction of oppositely charged ionogenic groups of the components and hydrophobic interactions of surfactant alkyl chains [1,2]. Binding of surfactant ions with oppositely charged linear polyelectrolytes proceeds as a cooperative process at a surfactant concentration above critical aggregation concentration (CAC) that is 1–3 orders of magnitude lower CMC [1,2]. Bound surfactant ions segregate inside polymer coil and form an intracomplex micelle. If the amount of surfactant ions in a system is not enough for the formation of a micelle inside each macroion, the non-uniform distribution of surfactant ions between macromolecules takes place [3]. In this case, complex particles of the constant composition, $\varphi_{\min}$, coexist with the free polyelectrolyte molecules. $\varphi_{\min}$ represents composition of PSC which comprises a micelle with a minimum (for the given experimental conditions) aggregation number, $n_{\min}$: $\varphi_{\min} = n_{\min}/n_{\mathrm{PE}}$ where n_{PE} is a number of polyelectrolyte monomer units incorporated into the complex particle [3,4]. Depending on the chemical nature of the polyelectrolyte, the values of $n_{\min}$ vary from tens to thousands. For example, $n_{\min}$ of alkyltrimethylammonium ions in the complexes with partially neutralized poly(acrylic acid) are close to the aggregation numbers of the spherical micelles of the corresponding surfactants in solution. In this case, molecularly dispersed PSC species comprising only one polyion

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were found in solution [4,5]. On the contrary, poly(diallyldimethylammonium chloride)−sodium dodecyl sulfate (PDADMAC−SDS) complexes are aggregated: each complex particle includes about 10^2 PE chains and $n_{\min}$ is about 10^5 [4]. In contrast to aggregation of "free" synthetic polyelectrolytes in poor solvents that make them insoluble [6], aggregation of PSC species in aqueous solutions is considered to result in the formation of water-soluble PSCs because no macro-phase separation is observed upon long keeping of PSC solutions. Moreover, such aggregated PSC species are characterized by a certain molecular mass and size [4]. Thus, molecularly dispersed and highly aggregated PSCs could be considered as two different types of PSC supramolecular organization in aqueous solutions. The reasons why for some systems the values of $n_{\min}$ are close to that for spherical surfactant micelles and molecularly dispersed PSCs are formed while for the others $n_{\min}$ is about 10^5 and the formation of complexes is accompanied by aggregation of PE macromolecules are still not clear.

This work presents the study of poly(*N*-ethyl-4-vinylpyridinium bromide)−sodium dodecyl sulfate complexes formation, phase state (soluble or insoluble in water−salt media), and supramolecular organization in salt containing aqueous solutions. In this work, we found PE/S pair for which either molecularly dispersed or aggregated complexes could be obtained and revealed some factors that control PSC supramolecular organization in aqueous solutions.

2. Experimental section

2.1. Materials

Three poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVP) samples with weight-average degree of polymerization $P_w = 570$ ($PEVP_{570}$), $P_w = 1200$ ($PEVP_{1200}$), and $P_w = 2350$ ($PEVP_{2350}$) were prepared by quaternization of poly(4-vinylpyridinium) fractions (obtained from Aldrich, Polymer Source Inc. and Polyscience Inc., respectively) with ethyl bromide in methanol at 60 °C [7]. According to IR and UV spectroscopy data, the degree of quaternization was $90 \pm 5\%$ for $PEVP_{570}$ and $83 \pm 5\%$ for $PEVP_{1200}$ and $PEVP_{2350}$. PEVP concentration in solution was determined by absorbance at $\lambda_{MAX} = 257$ nm by photometer "Hitachi 150-20" (Japan). Concentration of PEVP in the samples was from 2.5 mM to 25 mM. Hereafter, concentration of PEVP is given per mole of monomer (quaternized or not) units.

Sodium dodecyl sulfate (Serva) and oil-soluble dye Oil Yellow OB (Tokyo Casei Inc., Japan) were used without further purification.

2.2. Preparation of the samples

PEVP−SDS complexes were prepared by the addition of aqueous SDS stock solution to PEVP solution in the presence of 50 mM NaBr or NaCl at vigorous stirring. Insoluble complexes were separated from supernatant by the centrifuge "Hettich Zentrifugen Macro 12-24" (Germany) at 12,000 rpm. Residuary fine precipitates were removed from supernatant by filtration through membrane filters "Millipore", pore size 0.8 μm. Solutions before studies were kept for at least 24 h. Dilutions of the samples for static light scattering measurements were carried out directly before measurements.

The reaction mixture composition, Z, is determined as a ratio of SDS molar concentration to the total molar concentration of PEVP monomer units (quaternized or not): $Z = [SDS]/[PEVP]$. The composition of PSC, φ, is determined as a ratio of SDS ions number (n_S) to the total number of PEVP monomer units (n_{PE}) incorporated into the complex: $\varphi = n_S/n_{PE}$. It is clear that φ is equal to Z if surfactant ions are uniformly distributed between PE molecules and concentration of free S ions in solution is negligible in comparison with the total surfactant concentration in the system.

2.3. Methods

2.3.1. Determination of CAC value

Weighted quantities of Oil Yellow OB (0.5 mg per 1 ml of solution) were added to solutions of PEVP, $[PEVP] = 2.5$ mM, in the presence of different quantities of SDS, $10^{-6}\,M < [SDS] < 10^{-3}\,M$. Such quantity of the dye does not affect phase state of the complexes providing, at the same time, necessary excess of the dye in the system. To attain the equilibrium state, the samples were kept at 20 °C until absorbance at 346 nm remains unchanged for a week. Starting with a certain SDS concentration, the progressive increase of the absorbance is observed. This SDS concentration was accepted as CAC.

2.3.2. Turbidimetric titration

Turbidimetric titration was carried out using Specord M40 spectrophotometer (Germany) or "Hitachi 150-20" (Japan) or "Perkin Elmer Lambda EZ201" (USA) at $\lambda = 540$ nm. Turbidity of solutions was calculated as $T = (T_o - T_s)/T_o$ where T_o is light transmission of the initial PEVP solution, and T_s is light transmission of the complex solution.

The fraction, F, of PEVP included into PSC precipitate was calculated as follows:

$$F = ([PEVP]_o - [PEVP]_{sup})/[PEVP]_o$$

where $[PEVP]_o$ is the initial PEVP concentration in solution, and $[PEVP]_{sup}$ is PEVP concentration in the supernatant after separation of the precipitate.

2.3.3. Elemental analysis

Elemental analyses of PSC precipitates were carried out with "KARLO ERBA 1106" analyzer (Italy). Absolute error of S and N determination did not exceed 0.1 wt%. The molar ratio S/N is equal to the complex composition, φ.

2.3.4. High-speed sedimentation

High-speed sedimentation studies were carried out in the presence of 0.05 M NaCl using "Spinco-E" (Beckman, USA) ultracentrifuge supplied with Filpot−Swenson optical system for refractive index gradient determination. Rotation frequency (ω) was 48,000 rpm. The values of sedimentation coefficients (S) were calculated as described earlier [5] and expressed in Svedberg units (Sv), 1 Sv = 10^{-13} s. The experimental error of sedimentation coefficient determination was about 10–15%.

2.3.5. Laser light scattering

Molecular characteristics of water-soluble PSCs were obtained by static light scattering (SLS) using small-angle laser photometer KMX-6/DC (Milton Roy, USA) equipped with a 5 mW He–Ne laser as a light source ($\lambda = 633$ nm, the scattering angle $\theta = 6.5^\circ$) or laser light scattering goniometer "ALV-5" (ALV, Germany) with 10 mW He–Ne laser as a light source ($\lambda = 633$ nm, the scattering angle from 30° to 150°). The refractive index increments (dn/dc) were measured using KMX-16 differential refractometer (Milton Roy, USA) with 0.5 mW He–Ne laser as a light source ($\lambda = 633$ nm). The solvent (50 mM NaBr) equilibrated with PEVP or complex solution by dialysis was used as the reference sample. Weight-average molecular masses (M_w) were determined according to Debye equation or double Zimm extrapolation method. Linear dependencies of Kc/R_θ vs. concentration (c), and $(Kc/R_\theta)_{c\to o}$ and $(Kc/R_\theta)_{\theta\to 0}$ indicate that under the experimental conditions the dimensions and molecular masses of the scattering particles remain constant.

The average numbers of PEVP *chains* (N_{PE}) and SDS ions (n_S) in a particle of a soluble PSC were calculated as follows [4]:

$$N_{PE} = \frac{M_w}{P_w(0.83M_{PEVPBr} + 0.17M_{PVP} + \varphi M_{SDS} - \varphi A_{Na} - \varphi A_{Br})} \tag{1}$$

$$n_S = \varphi P_w N_{PE} \tag{2}$$

where M_w is molecular mass of PSC particles obtained from light scattering measurements, P_w is PEVP weight-average polymerization degree, M_{PEVPBr} is the molecular mass of quaternized monomer unit, M_{PVP} is molecular mass of non-quaternized poly(4-vinylpyridinium) monomer unit, M_{SDS} is the molecular mass of SDS, A_{Na}, and A_{Br} are the atomic masses of the counterions released on complexation. Coefficients "0.83" and "0.17" consider the degree of PEVP quaternization.

Diffusion coefficients (D_z) were determined by dynamic laser light scattering (DLS). Autocorrelation functions of the scattered light intensity fluctuations were measured using a 288-channel logic correlator "PhotoCor FC" (PhotoCor, USA). The obtained data were processed by cumulant and Tikhonov regularization methods. Apparent hydrodynamic radiuses (R_{app}) and average hydrodynamic radiuses (R_h) of appropriate equivalent spheres were calculated by the Stokes equation using the value of diffusion coefficient (D_z) measured at a certain concentration (D_{app}) or the value of D_z extrapolated to zero concentration, $(D_z)_o$, correspondingly.

Before light scattering measurements, all solutions were purified from the dust by filtration through membrane filter "Millipore" with a pore size of 0.45 μm.

All studies were carried out at 20 °C.

3. Results and discussion

3.1. Formation of complexes

It is well known that cooperative binding of PEs with oppositely charged S ions starts at a surfactant concentration above critical aggregation concentration (CAC) and is accompanied by segregation of S ions into intracomplex micelle which is capable to solubilize different organic compounds. The value of CAC can be estimated by solubilization of water-insoluble dye, e.g. Oil Yellow OB. Solubilization of this dye by PSCs and its influence on CAC value is well known [8,9]. Fig. 1 shows that CAC value in PEVP–SDS mixtures is about 5×10^{-5} M SDS. Binding of SDS with PEVP of high degrees of quaternization (more than 50%) is known to be highly cooperative above CAC either in salt or salt-free solutions [10] and at relatively low Z ($Z \leq 0.5$) concentration of free S ions in solution was shown to be close to CAC [10]. In our experimental conditions, total SDS concentration in solution is no less than 10^{-3} M. Consequently, concentration of free S ions is negligible in comparison with the total SDS concentration in the system. Therefore, we accepted that in our experiments all surfactant ions are incorporated into a complex with PEVP.

PSCs can be soluble or insoluble in aqueous media depending on pH, ionic strength, chemical nature of the components, etc. [2–5]. It was found that polycation polymerization degree affects PSC solubility by the decisive way. Indeed, addition of even small quantity of SDS to a solution of $PEVP_{570}$ results in the significant increase of turbidity (Fig. 2, curve 1). $PEVP_{570}$ fraction in the precipitate also rises (Fig. 3, curve 1). It means that in the whole range of Z studied ($0 < Z \leq 1$) only insoluble $PEVP_{570}$–SDS complexes are formed.

On the contrary, $PEVP_{1200}$ and $PEVP_{2350}$ solutions remain externally homogeneous up to $Z \approx 0.45$ (Fig. 2). Further addition of SDS leads to a sharp increase of turbidity due to insoluble complex precipitation.

Fig. 3 shows the dependencies of the fraction of PEVP included in the precipitate (F) as a function of Z. It is clear that all PEVP (P_w = 1200 and 2350) remains in the solution until Z

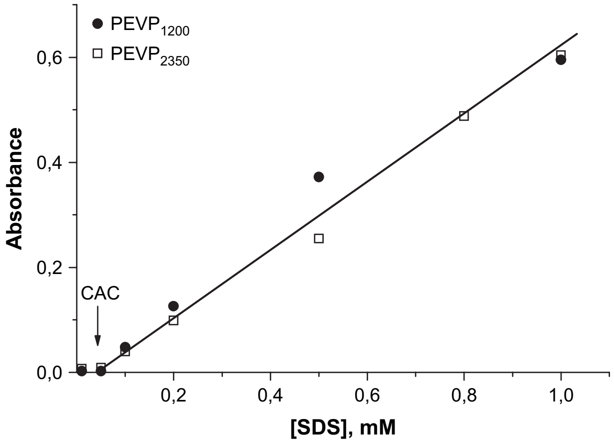

Fig. 1. UV absorbance of PEVP solutions containing Oil Yellow OB vs. SDS concentration; [PEVP] = 2.5 mM, [NaBr] = 50 mM, $\lambda = 346$ nm.

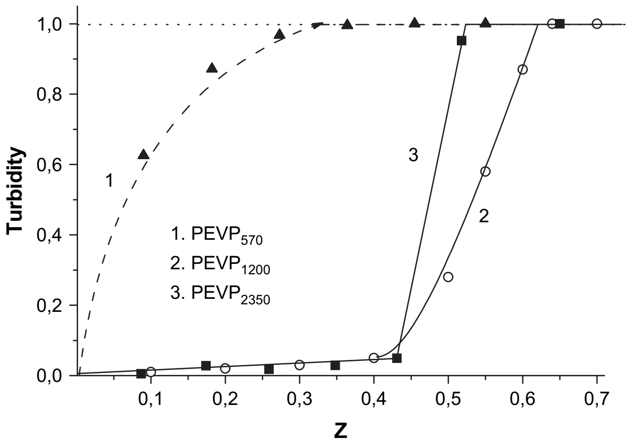

Fig. 2. Curves of turbidimetric titration of PEVP solutions with SDS; $[PEVP]_o = 25$ mM, $[NaBr] = 50$ mM.

approaches the critical value, Z_c, marked by an arrow in Fig. 3. The value of Z_c is the same for both PEVP fractions and equals to 0.45. When Z exceeds Z_c, phase separation occurs. $F(Z)$ functions are extrapolated to $\varphi = Z = 1$ for PEVP$_{570}$, $\varphi = Z = 0.9$ for PEVP$_{1200}$, and $\varphi = Z = 0.7$ for PEVP$_{2350}$. Taking into account that the degree of quaternization is 90 ± 5% for PEVP$_{570}$, and 83 ± 5% for PEVP$_{1200}$ and PEVP$_{2350}$, the ratio of the components in insoluble PSCs is close to charge-to-charge stoichiometry. Indeed, it was confirmed by the elemental analysis data (Table 1) that in insoluble PEVP–SDS complexes each quaternized PEVP unit corresponds to one SDS ion. The constant values of S/N ratio indicates that composition of insoluble complexes is independent of Z.

Similar results are obtained in the presence of 50 mM NaCl except for a slightly higher value of Z_c. Fig. 4 shows F vs. Z dependencies obtained in the presence of NaCl or NaBr for PEVP$_{2350}$ as an example. We believe that such influence of the chemical nature of supporting electrolyte is caused by partial substitution of PEVP counterions, Br^- ions, to Cl^- ions. Such substitution increases lyophilizing ability of free PEVP units [11]. As a result, slight extension of the region of water-soluble PSC existence is observed.

Table 1
The data of elemental analysis of insoluble PSCs

PEVP (P_w)	Z	S (wt%)	N (wt%)	$\varphi = S/N$ (mol/mol)	SO_4^-/N^+ (mol/mol)
1200	0.85	7.0 ± 0.1	3.7 ± 0.1	0.83 ± 0.03	1.0 ± 0.1
	0.65	7.4 ± 0.1	4.0 ± 0.1	0.81 ± 0.03	0.97 ± 0.08
2350	0.72	6.8 ± 0.1	4.2 ± 0.1	0.71 ± 0.03	0.86 ± 0.08
	0.65	6.7 ± 0.1	4.0 ± 0.1	0.73 ± 0.03	0.88 ± 0.09

It should be emphasized that Z_c values are invariable in the whole range of PEVP concentrations studied. For instance, comparison of the curve 3 on Fig. 3 with curve 1 on Fig. 4 shows that twofold decrease of PEVP concentration does not affect the value of Z_c.

Solutions of PEVP–SDS complexes in the presence of 0.05 M NaCl were studied by the high-speed sedimentation technique. Fig. 5 shows some sedimentation profiles of PEVP$_{1200}$–SDS and PEVP$_{2350}$–SDS solutions. Sedimentation coefficients are presented in Table 2. The similar sedimentation patterns were obtained also for the lower PEVP concentration, $[PEVP] = 10$ mM (the data are not shown).

It is clear that formation of complexes upon addition of SDS into the reaction mixture is accompanied by appearance of the second "fast" sedimentation peak indicating appearance of the species of another type in the system. Comparison of the sedimentation coefficients with those for the "free" PEVP (Table 2) indicates that the 'slow' peaks correspond to sedimentation of free polyions, while the "fast" peaks are due to sedimentation of the soluble PSCs. The above results show that the bound surfactant ions are non-uniformly distributed between the PE chains. The reason of such disproportionation consists in the formation of an intracomplex micelle characterized by a certain value of n_{min} [4,5]. If the amount of S ions in a system is not enough for formation of the micelles of a minimal size inside each macromolecule ($Z < Z_{min}$) PSC species of a constant minimal composition $\varphi = \varphi_{min}$ coexist in solution with free PE molecules (region 1 on Fig. 6). At $Z = Z_{min}$ micelles of a minimal size are formed inside all PEVP

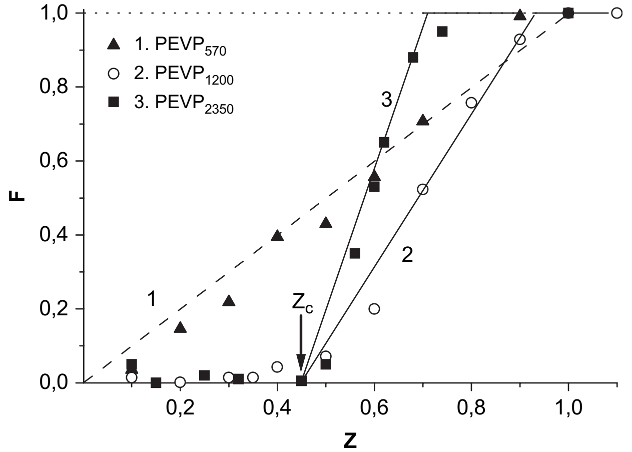

Fig. 3. PEVP fraction in precipitate (F) as a function of the reaction mixture composition, Z; $[PEVP]_o = 25$ mM, $[NaBr] = 50$ mM.

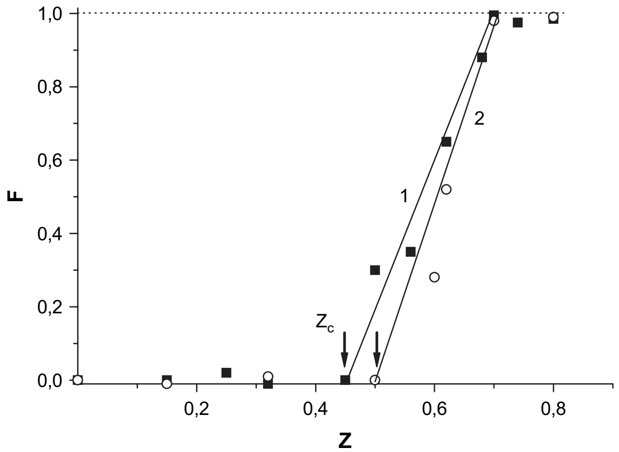

Fig. 4. Relative PEVP$_{2350}$ fraction in the precipitate (F) as a function of Z in the presence of 50 mM NaBr (1) or NaCl (2); $[PEVP]_o = 10$ mM.

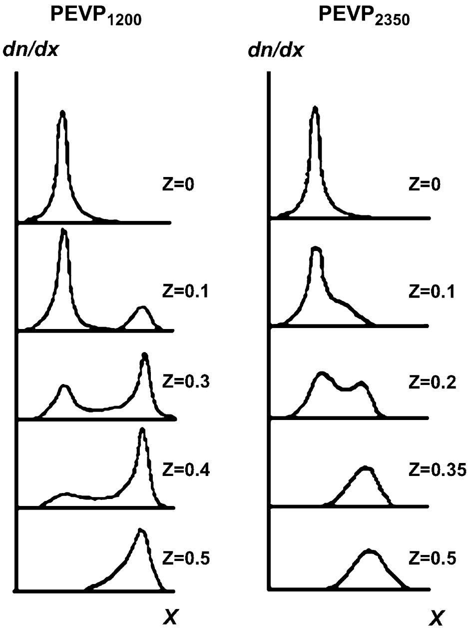

Fig. 5. Sedimentation profiles for free PEVP ($Z = 0$) and PEVP–SDS complexes at different Z; [PEVP] = 20 mM, [NaCl] = 50 mM, and $t = 50$ min.

Table 2
Sedimentation coefficients for free PEVP and PEVP–SDS complexes at different Z; [NaCl] = 50 mM, [PEVP] = 20 mM

Z	$PEVP_{1200}$		$PEVP_{2350}$	
	S_1 (Sv)	S_2 (Sv)	S_1 (Sv)	S_2 (Sv)
0	1.3	–	2.0	–
0.1	1.8	5.5	ND[a]	ND[a]
0.2	1.5	5.8	2.2	3.5
0.35			–	4.1
0.4	1.5	5.7	–	4.7
0.5	–	6.6	–	5.5
0.6[b]	–	6.0		5.6

[a] ND – not determined because of the poor resolution of sedimentation peaks.

[b] Supernatant after separation of PSC precipitate.

molecules, and only one peak attributed to sedimentation of PSC particles of $\varphi_{\min}$ is observed ($Z = 0.5$ for $PEVP_{1200}$ and $Z = 0.35$ for $PEVP_{2350}$, Fig. 5). In general case, further increase of S ions content in the reaction mixture ($Z_{\min} < Z < Z_c$) should result in the even distribution of S ions between PE molecules and formation of a single type of PSC species of $\varphi = Z$ (region 2 on Fig. 6). However, the extension and even the existence of the region 2 depends, in particular, on the PE polymerization degree, because the value of $\varphi_{\min}$ is determined by P_w [3]. Indeed, the values of φ_c and $\varphi_{\min}$ presented in Table 3 indicate the evident difference between PEVP fractions from this point of view.

In the case of $PEVP_{2350}$–SDS complexes, the value of $Z_{\min}$ equals to 0.35 and there is a region $Z_{\min} \le Z \le Z_c$ (region 2 on Fig. 6) in which composition of water-soluble complexes coincides with Z and, therefore, can be varied. On the contrary, in the case of $PEVP_{1200}$–SDS complexes, Z_c coincides with $Z_{\min}$ (collapse of the region 2 on Fig. 6). Consequently, in the whole range of $0 < Z \le Z_c$, water-soluble $PEVP_{1200}$–SDS complexes have the solely possible composition of $\varphi_c = \varphi_{\min}$. The obtained results are in a good agreement with the concept that the value of $n_{\min}$ is independent of PE polymerization degree and $\varphi_{\min}$ depends on P_w as $\varphi_{\min} = n_{\min}/P_w$ [3]. On the basis of the obtained $\varphi_{\min}$ values, we estimated the values of $n_{\min}$ (Table 3). It should be noted that $n_{\min}$ value estimated in such a way represents a minimum aggregation number of the intracomplex micelle in the case of molecularly dispersed PSCs and the average quantity of the surfactant ions per polymer molecule in the case of aggregated PSCs. It is clear that the values of $n_{\min}$ are actually similar for both PEVP samples being about 10 times higher than that for the free SDS spherical micelles in solution (about 70 SDS ions [12]). Moreover, it seems that just such relatively high $n_{\min}$ value is the reason of impossibility of $PEVP_{570}$–SDS soluble complex formation. Indeed, in the latter case, $n_{\min}$ is lower than PEVP polymerization degree and there are no free PE units to provide solubility of PSC species. The similar results were described earlier for the complexes of partially neutralized poly(acrylic acid) and cationic surfactants [3].

The value of Z_c is determined by hydrophilic/hydrophobic balance of PSC species. For the complexes formed by the same PE/S pair, Z_c value is controlled by the portion of PE units bound with the surfactant ions, i.e. by the complex composition. Therefore, the value of Z_c is independent of PEVP polymerization degree and at $Z > Z_c$ phase separation is observed for the both PEVP–SDS complex solutions (Fig. 6, region 3). The data of elemental analysis (Table 1) and sedimentation data (Table 2) show that phase separation is accompanied by the second disproportionation: PSC species of the critical composition, φ_c, coexist in solution with the precipitate of insoluble PSC whose composition is close to charge-to-charge stoichiometry. Similar results were described earlier

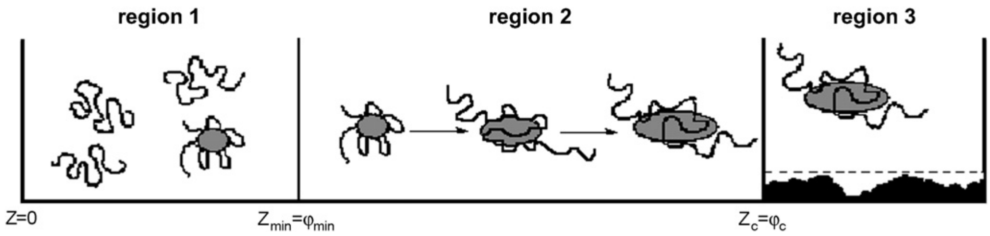

Fig. 6. General scheme of PSC formation.

Table 3
The values of critical (φ_c) and minimal (φ_{min}) PSC compositions in water–salt media

Supporting electrolyte (50 mM)	$PEVP_{1200}$–SDS			$PEVP_{2350}$–SDS		
	$\varphi_c = Z_c$	$\varphi_{min} = Z_{min}$[a]	$n_{min} = P_w\varphi_{min}$	$\varphi_c = Z_c$	$\varphi_{min} = Z_{min}$[a]	$n_{min} = P_w\varphi_{min}$
NaCl	0.5	0.5	600	0.5	0.35	800
NaBr	0.45			0.45		

[a] According to the high-speed sedimentation data.

for the complexes of poly(acrylic acid) with cationic surfactants [5].

One more remark should be done concerning the results of sedimentation. Surprisingly, it was found that sedimentation coefficients of PSCs formed by $PEVP_{2350}$ are slightly lower than that for $PEVP_{1200}$–SDS complexes. In order to elucidate the situation, water-soluble complexes were studied by static and dynamic laser light scattering in the presence of 50 mM NaBr. Unfortunately, it is impossible to carry out sedimentation studies in the presence of NaBr because of the great difference between atomic weights of the ions that causes a strong distortion of sedimentation pattern. From the other side, partial substitution of Br^- counterions to Cl^- ions should be taken into account upon static light scattering studies because of the great difference between atomic masses of the ions. Determination of the substitution extent is a special problem that was not solved in the frame of this work. For our subsequent light scattering studies, we accepted that in 50 mM NaBr the value of φ_{min} equals to 0.45 for $PEVP_{1200}$–SDS complexes and 0.35 for $PEVP_{2350}$–SDS complexes.

3.2. Macromolecular organization of PEVP–SDS complexes in solution

Fig. 7 shows particle size distributions for free PEVP and PEVP–SDS complexes reconstructed from corresponding autocorrelation functions. It is clear that at $Z \leq 0.4$ the size of $PEVP_{2350}$–SDS complex species is close to that for the free $PEVP_{2350}$ molecule (Fig. 7a distributions 2 and 3). Increase of φ up to $\varphi = Z = 0.45$ leads to appearance of the second mode on the particle size distributions (Fig. 7a (4)). On the contrary, for $PEVP_{1200}$–SDS complexes, the presence of the second mode on the particle size distributions is observed in the whole range of Z corresponding to the formation of soluble PSCs, and even at $Z = 0.1$ at which PSC species of $\varphi = 0.45$ coexist in solution with free PEVP molecules (Fig. 7b). It is not surprising because in the latter case soluble complexes have the solely possible composition of $Z = 0.45$ in the whole range of $Z \leq Z_c$. Quite similar behavior was shown earlier for PDADMAC–SDS complexes in diluted aqueous-salt solutions [4]. It was shown that in the whole range of Z corresponding to

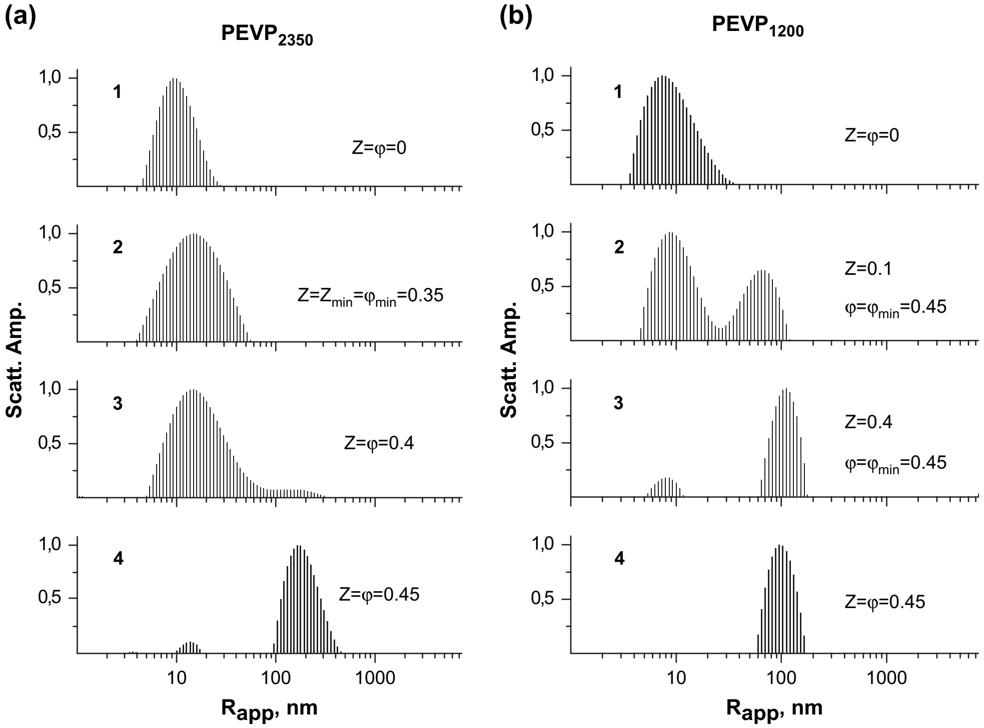

Fig. 7. Particle size distributions for the free PEVP (1) and PEVP–SDS complexes at different Z; [PEVP] = 20 mM (1–3); [PEVP] = 5 mM (4); [NaBr] = 50 mM, $\theta = 90°$.

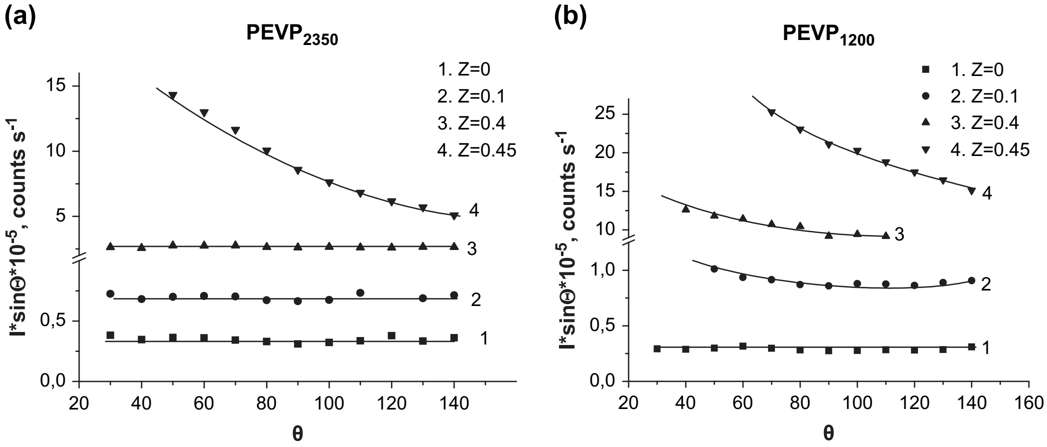

Fig. 8. Scattering indicatrices for free PEVP (1) and PEVP–SDS complexes at different Z; [PEVP] = 20 mM (1–3); [PEVP] = 5 mM (4), [NaBr] = 50 mM.

the formation of soluble complexes, only aggregated complexes of the constant composition $\varphi_{\min} = \varphi_c = 0.4$ are formed [4].

It should be noted that appearance of the second mode on the particle size distributions in all cases is accompanied by increase of the scattered light intensity and appearance of asymmetry of the scattering indicatrices (Fig. 8) indicating formation of “large” particles in solutions. The size of such complex species ($R_{app} \approx 100–120$ nm) is approximately 10 times higher than the size of the free PEVP coil ($R_{app} = 10–12$ nm). The constant values of diffusion coefficients that do not depend on the scattering angle (the data are not shown) confirm translational nature of each dynamic mode for all samples studied. Consequently, the slow mode corresponding to $R_{app} \approx 100–120$ nm appears to relate to aggregated PSC species, while the fast mode ($R_{app} \approx 10–12$ nm) should be attributed either to molecularly dispersed PSC species (Fig. 7a, distributions 2–4) or to the free PEVP molecules (Fig. 7b, distributions 1–3) because according to the sedimentation data there is no free PEVP$_{2350}$ at $Z \geq 0.35$ while for PEVP$_{1200}$, free PEVP coexists with PSC species at $Z < 0.45$.

Molecular characteristics of PSCs were determined by SLS (Figs. 9 and 10). The results of DLS and SLS studies are summarized in Table 4. It is seen that molecular mass of molecularly dispersed PSCs formed by PEVP$_{2350}$ at $Z \leq 0.4$ is equal to 7×10^5 g mol^{-1}. Molecular mass of aggregated complex species determined for PEVP$_{1200}$–SDS complexes at $Z = 0.45$ and even at $Z = 0.4$ is about 1.2×10^7 g mol^{-1} that is about 50 times higher than that for free PEVP$_{1200}$. It should be emphasized that in PEVP$_{1200}$–SDS mixture at $Z = 0.4$, PSC species coexist in solution with free PEVP molecules. However, we neglected contribution of free PEVP molecules into the total intensity of the scattered light because it is known that contribution of the particles into a total intensity of scattered light depends on their size as $I \sim R^4–R^6$ [13]. Therefore, contribution of “small” free PEVP molecules ($R_{app} \approx 10$ nm) in the average scattered light intensity is significantly lower than contribution of large PSC species ($R_{app} \approx 100$ nm) even at $Z = 0.4$. Concentration of the scattering particles was calculated as the mass concentration of the complex of $\varphi_{\min} = 0.45$ we know to form under the given conditions. In order to insure that dilution does not cause any alteration of PSC characteristics, we specially controlled that the scattered light intensity remains unvaried after complete indicatrix measurement for each PSC concentration. It should be noted that molecular mass of PSC particles obtained in such a way is understated.

From the obtained M_w values, the average number of the polyelectrolyte chains, N_{PE}, and the average number of surfactant ions, n_S, incorporated into a complex particle have been calculated. The presented data (Table 4) show that “large” particles are actually aggregated PSC species comprising about 40 macromolecules and 20,000 surfactant ions while molecularly dispersed complex particle does include only one PEVP molecule and about 900 SDS ions. In the latter case, the value of the average hydrodynamic radius (R_h) reduces from 19 nm for free PEVP to about 12 nm for PEVP$_{2350}$–SDS complex, $\varphi = 0.4$. It means that complex formation induces some compactization (collapse) of PEVP coil accompanying by significant decrease of A_2 value (Table 4) due to increased hydrophobicity of PSC species in comparison with free PEVP molecule. Collapse of PE coils was shown earlier for some

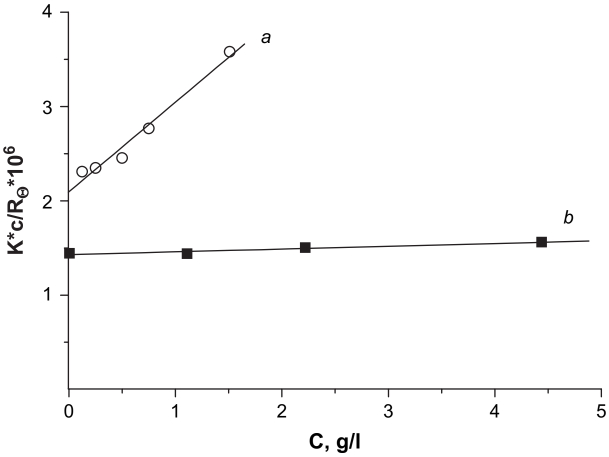

Fig. 9. Kc/R_θ vs. concentration for solution of free PEVP$_{2350}$ (a) and its complex with SDS at $Z = 0.4$ (b), [NaBr] = 50 mM, $\theta = 6.5°$.

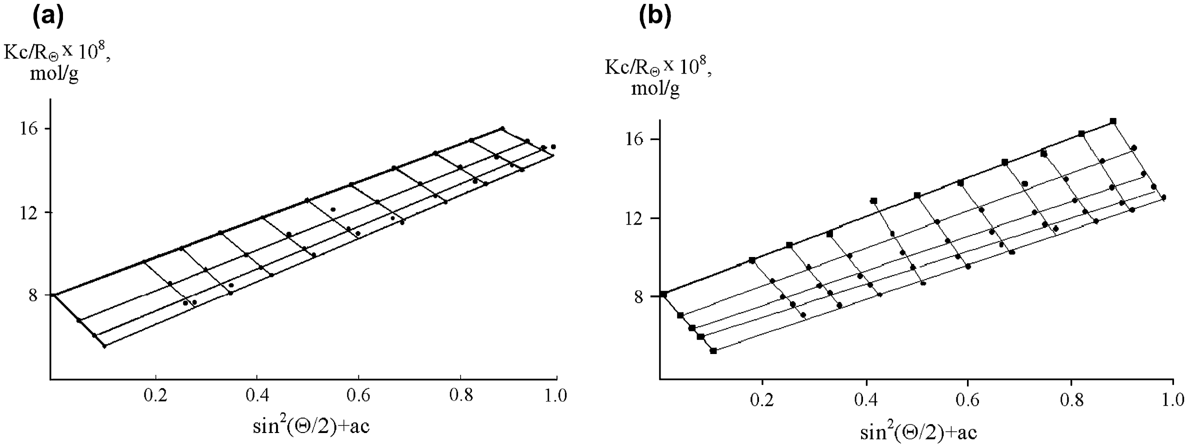

Fig. 10. Zimm diagram for $PEVP_{1200}$–SDS complexes, $Z = 0.4$ (a); $Z = 0.45$ (b), [NaBr] = 50 mM, $a = 0.042$ (a) and 0.07 (b).

polyelectrolyte–surfactant systems and was attributed to hydrophobization of PE chain upon binding of S ions [14,15]. At the same time, aggregation of PE molecules accompanying formation of PSCs in the case of $PEVP_{1200}$–SDS system impedes any studies of a single PEVP coil size by means of DLS.

The results of light scattering clearly elucidate the reasons of the difference between sedimentation coefficients for the complexes formed by different PEVP fractions. Indeed, at $Z < 0.45$ $PEVP_{2350}$–SDS complexes are molecularly dispersed and their sedimentation coefficients are relatively small in comparison with that of aggregated $PEVP_{1200}$–SDS species. Aggregation of $PEVP_{2350}$–SDS complexes at $Z = 0.45$ leads to significant increase of their molecular mass and, consequently, of their sedimentation coefficients that become similar to that for aggregated $PEVP_{1200}$–SDS complexes.

The obtained results show that both molecularly dispersed and highly aggregated complexes can be obtained in aqueous solutions for the polymers of the same chemical nature. Moreover, both types of PSC supramolecular organization can be realized even for the same polymer. We believe that the reason for this is that the increase of PSC composition leads to hydrophobization of PSC species that causes their aggregation in solution. If hydrophobicity of the complex species remains unvaried upon change of the reaction mixture composition (as it is for $PEVP_{1200}$–SDS and PDADMAC-SDS [4]), supramolecular organization of the complexes also remains constant in the whole range of Z. Such assumption is in a good agreement with our recent studies showing that hydrophobization of PSC complexes by solubilization of organic additives also causes PSC aggregation while hydrophilization, on the contrary, leads to their complete disaggregation but not destruction [16–18].

4. Conclusions

Two types of supramolecular organization of PEVP–SDS complexes in water–salt media were found. It was shown that aggregation state of PSC species is determined by the complex composition which, in its turn, depends on PEVP polymerization degree and the reaction mixture composition. When PEVP polymerization degree is significantly higher than $n_{\min}$ and about 60% of PEVP units in the complex species are free ($PEVP_{2350}$, $Z < 0.45$), formation of molecularly dispersed complexes comprising one PEVP molecule and about 900 SDS ions is observed. Hydrophobization of $PEVP_{2350}$–SDS complex species upon increase of their composition up to $Z = 0.45$ leads to formation of the aggregates. In the case of soluble $PEVP_{1200}$–SDS complexes which have the constant composition of $\varphi_{\min} = \varphi_c = 0.45$, formation of aggregated PSCs comprising about 40 macromolecules and 20,000 surfactant ions is observed in the whole range of $Z < Z_c$. If PEVP polymerization degree is close to $n_{\min}$ (as it is in the case of $PEVP_{570}$) and there are no free PE units to provide complex solubility even at $\varphi_{\min}$, only water-insoluble PSCs are formed.

Table 4
Molecular characteristics of free PEVP and PEVP–SDS complexes

PEVP (P_w)	Sample	$M_w \times 10^{-3}$ (g mol^{-1})	N_{PE}	n_S	$(D_z)_o \times 10^7$ (cm s^{-1})	R_h (nm)	R_{app} (nm)	A_2 (mol sm^3 g^{-2})
2350	PEVP, $Z = 0$	460	1	–	1.11	19	12[a]	4.4×10^{-4}
	PSC, $Z = 0.4$	704	1.07	900	1.73	12.5	12[a]	1.4×10^{-5}
	PSC, $Z = 0.45$						120[b]	
1200	PEVP, $Z = 0$	240	1		1.53	14	10[a]	8.74×10^{-4}
	PSC, $Z = 0.4$	12,400	38	20,000			120[a]	-8.05×10^{-9}
	PSC, $Z = 0.45$	12,300	37	20,000			120[b]	-1.02×10^{-8}

[a] [PEVP] = 20 mM.
[b] [PEVP] = 5 mM.

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