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Aggregation of Ionic Amphiphils in Dilute Solutions Controlled by Oppositely Charged Polyelectolyte Templates

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Summary: Formation and structure of water-soluble complexes of poly(acrylic acid) (PA) and poly(diallyldimethylammonium chloride) (PDADMAC) with oppositely charged surfactants have been studied by elastic and quasi-elastic laser light-scattering and high-speed sedimentation technique. It was experimentally shown that generation of intracomplex micellar phase is the necessary condition for formation of such complexes. Minimum aggregation number of the surfactant ions in the complex micelle was found to be determined by the chemical nature of the polymer.

Keywords: micellar phase; minimum aggregation number; polyelectrolyte-surfactant complexes

Introduction

It is known that ionic surfactants are bound to oppositely charged polyions in water solution at concentrations 2-3 orders of magnitude lower than cmc to form a micellar phase incorporated in polyelectrolyte-surfactant complexes (PSCs)[1]. However, the effect of polyionic templates is not limited by the above phenomenon. Polyions depending on their structure can also control a minimum aggregation number and the structure of the micellar species in dilute and semi-dilute polyelectrolyte solutions [2-4]

The present work is devoted to the study of the minimum aggregation number of the surfactant ions in micelles of polyelectrolyte-surfactant complexes (PSC), with the special interest on the influence of polyelectrolyte nature on the structure of PSC particles.

Experimental Section

Synthesis and fractionation of poly(acrylic acid) (PA) were described elsewhere [5]. Fraction of PA with weight average degree of polymerization of P_w=600 was used. Poly(diallyldimethylammonium chloride) (PDADMAC) with weight-average molecular

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mass, M_w = 460000, supplied as an aqueous solution, C = 35.4 wt % by CPS Chemical Company, Inc. as Agerfloc WT 35 VHV was used. Surfactants – tetradecyltrimethylammonium bromide ($C_{14}AB$) (Aldrich-Chemie, Germany) and sodium dodecyl sulfate (SDS) (Serva) were used without further purification.

The high-speed sedimentation studies were carried out at 20°C in the presence of 0.1 M NaCl with a Spinco-E (Beckman, USA) ultracentrifuge supplied with Filpot-Swenson optical system for the refractive index gradient determination. Rotation frequency was 58000 rpm. Molecular characteristics of water-soluble complexes were obtained by static light scattering with small-angle laser photometer KMX-6/DC (MILTON ROY, USA) with 4 mW He–Ne laser as a light source (λ=630 nm., the scattering angle 6.5°.) or with ALV-5 laser goniometer (ALV, Germany) in the range of scattering angles from 30° to 150° with 25 mW He-Ne laser, λ= 630 nm. as the light source. The refractive index increment *(dn/dc)* was measured using KMX-16 differential refractometer (MILTON ROY, USA) with 0.5 mW He–Ne laser as a light source (λ=630 nm.). The solvent equilibrated with the complex solution by dialysis was used as the reference sample. For all studied systems the dependence of (Kc / R_θ) vs. c obey the Debye equation, indicating that at the experimental conditions the dimension and the molecular weight of the PSC particles remains constant as PSC concentration decreases. Autocorrelation functions of scattered light intensity fluctuations were measured using FotoKorr-M 72-channel correlator. The obtained data were processed by the cumulant method Average hydrodynamic radii of appropriate equivalent spheres *(Re)* were calculated using the Stokes equation.

The reaction mixture composition Z is determined as the ratio of surfactant (S) molar concentration to the molar concentration of polyelectrolyte (PE) monomer units in the solution Z=[S]/[PE]. The composition of PSC, φ, is determined as the ratio of the number of surfactant ions to the number of polyion units in the complex particle $\varphi=[S]_{psc}/[PE]_{psc}$.

All investigations were performed at T=20°C. PA-$C_{14}TAB$ complexes were studied at pH=5.7.

Results and Discussion

The homogeneous mixtures of PA or PDADMAC with oppositely charged surfactants have been studied by high-speed sedimentation technique in the range of Z where formation of insoluble PSCs is not observed. Figure 1 represents the sedimentation profiles of the studied mixtures. In the range of Z values from 0 to 0.15 for PA-$C_{14}AB$ and from 0 to 0.4 for PDADMAC-SDS mixtures respectively, two peaks are observed. The existence of two peaks

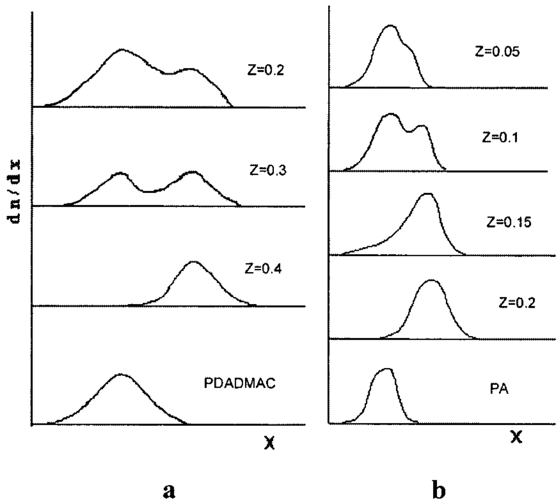

Figure 1. Sedimentation profiles for PDADMAC-SDS (a) and PA and PA-$C_{14}AB$ (b) mixtures.

Table 1. Sedimentation coefficients (S) for free polyelectrolytes and PSCs.

PA-C_{14}AB			**PDADMAC-SDS**		
Z	**$S_1 x10^{13}$, s**	**$S_2 x10^{13}$, s**	**Z**	**$S_1 x10^{13}$, s**	**$S_2 x10^{13}$, s**
0	1.7	-	0	1.3	-
0.05	1.8	2.8	0.2	1.3	3.5
0.10	1.7	2.7	0.3	1.2	3.7
0.15	-	2.8	0.4	-	3.5
0.20	-	3.1	0.5	-	3.8

on the sedimentograms unambiguously indicates that the both reaction mixtures contain two different types of particles. Comparison of calculated sedimentation coefficients with that of free PE (Table 1) shows that the "slow" peak corresponds to a free polyion, while the "fast" - to the soluble PSC species. The increase of the surfactant concentration in the reaction mixture is accompanied with decrease of the area of free PE peak and increase of the area of the PSC peak without change the values of corresponding sedimentation coefficients (Fig. 1 and Tab. 1). The above results indicate that binding of the surfactant ions to the PE chains is characterized with non-uniform distribution of the surfactant ions between PE chains (i.e. disproportionation). In this range of *Z*, PSC particles coexist with the free polyions. In other words, increase of *Z* results only in change of a mass ratio between free PE and water-soluble

PSCs of a constant composition, $\varphi=\varphi_{min}$. Therefore, we may conclude that in such PSC particles the surfactant ions incorporated in PSC species form micelles of the minimum size, i.e of the minimum aggregation number (n_{min}) required for existing of a micellar phase at the experimental conditions. The existence of only one peak attributed to sedimentation of PSC particles upon increasing Z up to Z_{min} (0.15 and 0.4 for PA-C_{14}AB and PDADMAC-SDS PSCs respectively) indicates that the concentration of the surfactant ions in solution finally becomes high enough to form a micelle of the minimum size bound to PE chain. Therefore, in order to obtain a homogeneous system containing only the complex species of the minimum composition, φ_{min}, Z value should be equal to Z_{min}.

For evaluation of the figure of n_{min}, the M_w values of PSCs were measured by elastic laser light scattering. The M_w of the PA-C_{14}AB complex was determined from low angle light scattering data at $\theta=6.5^o$ using the Debye extrapolation. The double Zimm extrapolation was used in the case of PDADMAC-SDS PSCs (Fig. 2). As it is seen, the $(Kc/R_\theta)_{c\to o}$ and $(Kc/R_\theta)_{\theta\to 0}$ dependencies are linear indicating that dilution does not induce any association or dissociation of PSC species within the whole concentration range ($3x10^{-4} > c > 5x10^{-5}$ g/ml).

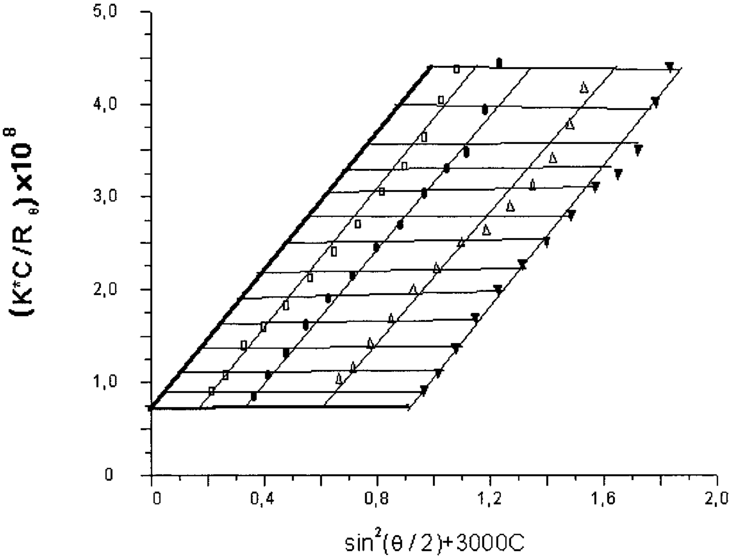

Figure 2. Zimm plot for PDADMAC-SDS system, C_{NaCl}=0.05M, Z=0.4.

From the obtained M_w values (Tab. 2), the average number of the polyelectrolyte chains, *N*, and the average number of surfactant ions, *n*, incorporated into the complex particle have been calculated [6]. The results are summarized in Table 2.

Table 2. Molecular characteristics of polyelectrolytes and PSCs (*N*-the number of PE molecules, *n*-the number of S-ions in PSC particle).

	Z	$\overline{M}_w$**x10^{-4}**	***N***	***n***	**$(D_Z)_0$x10^7, sm^2/s**	***Re*, nm**
PA	-	5.6	1	-	2.1	10
PSC PA-C_{14}AB	0.15	8.0	1	90	4.6	5
PDADMAC	-	46	1	-	1,0	37
PSC PDADMAC-SDS	0.4	1.1 10^4	150	1.7 10^5	0.24	89

The M_w value obtained obviously indicates that one particle of water soluble PA-C_{14}AB PSC, φ_{min}, contains only one PA chain and *ca.* 90 surfactant ions. It suggests that PA-surfactant interaction is not accompanied by polyelectrolyte association. Hence, PSC solutions may be considered as solution of individual complex molecules. The estimated n value is close to an aggregation number corresponding to spherical micelles which C_{14}AB forms in water solutions [7].

Entirely different situation has been observed for PDADMAC-SDS PSCs. The M_w of PSC species considerably exceeds the M_w of PDADMAC indicating aggregation of the PE chains. Moreover, the estimated n value by 3 order of magnitude exceeds the aggregation number of free SDS spherical micelles. Hence, in this case, the PE imposes on the micellar phase another morphology, not typical for the micelles of free surfactant.

Conclusions

Aggregation of the surfactant ions and generation of micellar phase is necessary condition for the formation of PSCs. Minimum aggregation numbers of the surfactant ions within PSC micelles were shown to be strongly dependent on the chemical nature of the polyelectrolyte. In the case of PA-C_{14}AB complexes n_{min} is close to that in the polymer-free surfactant solutions. On the contrary, in the case of PDADMAC-SDS complexes the n_{min} value is at least three orders of magnitude higher than for free SDS indicating formation of a micellar phase with absolutely different morphology.

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