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Self-Organization of Ionic Surfactants Controlled by Oppositely Charged Polyelectolytes

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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: tetradecyltrimethylammonium bromide and sodium dodecylsulfate correspondingly have been studied by elastic and quasi-elastic laser light-scattering, high-speed sedimentation and viscometry techniques. It was shown that minimum aggregation number of the surfactant ions in the complex micelle is controlled by the chemical nature of the polymer. A shift from dilute to semi-dilute solution regime with respect to a free polyelectrolyte results in drastic rearrangement in PDADMAC-SDS complex structure.

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

Introduction

It is known that ionic surfactants are bound to oppositely charged polyions in water solution at concentrations (cac) 2-3 order of magnitude lower than cmc of the free surfactants to form a micellar phase incorporated in polyelectrolyte-surfactant complexes (PSC)s[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 structure of the micellar species in dilute and semi-dilute polyelectrolyte solutions[2-4].

The present work is devoted to determination of the minimum aggregation numbers of the surfactant ions in micellar species incorporated in the PSCs, with the special interest in the influence of polyelectrolyte nature and its concentration regime on the structure of PSC particles in solution. Two varieties of PSC were studied: one formed by partly neutralized poly(acrylic acid)) (PA) and tetradecyltrimethylammonium bromide ($C_{14}AB$), another formed by poly(diallyldimethylammonium chloride) (PDADMAC) and sodium dodecylsulfate (SDS).

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Experimental Section.

Synthesis and fractionation of poly(acrylic acid) (PAA) were described elsewhere[5]. The fraction with weight average molecular mass M_w=4.3x10^4 (P_w=600) was used. Poly(diallyldimethylammonium chloride) (PDADMAC), M_w=4,6x10^5 (P_w of 3000) supplied by CPS Chemical Company, Inc. in the form of 35.4 wt % aqueous solution (Agerfloc WT 35 VHV) was used as purchased. $C_{14}AB$ (Aldrich-Chemie, Germany) and SDS (Serva) were used without further purification.

Molecular characteristics of water-soluble complexes were obtained by static light scattering with small-angle laser photometer KMX-6/DC (MILTON ROY, USA) equipped with 4 mW He–Ne laser (λ=630 nm., the scattering angle 6.5°) or with ALV-5 laser goniometer (ALV, Germany) equipped with 25 mW He-Ne laser, λ= 630 nm. as the light source in the range of scattering angles from 30° to 150°. 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. Diffusion coefficients (D_z) were determined by dynamic light scattering. Autocorrelation functions of scattered light intensity fluctuations were measured using FotoKorr-M 72-channel correlator. The obtained data were processed by the cumulant method and Tikhonov regularization. Average hydrodynamic radii of appropriate equivalent spheres *(Re)* were calculated using the Stokes equation.

The high-speed sedimentation studies were carried out at 20°C in the presence of 0.05-0.1M 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.

Rheological measurements were carried out in a Ubellode capillary viscometer with a suspended meniscus at 20°C; the samples were thermostated for 15 min prior to the measurements in the absence of added salt.

The reaction mixture composition Z was 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, was 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 measurements were performed at T=20°C. PA-C_{14}AB complexes were studied at pH=5.7-6.0.

Results and discussion

The solutions of studied PEs remain homogeneous upon addition of oppositely charged surfactants until Z approaches a certain critical value Z_c. Then phase separation is observed due to formation of the insoluble PSCs. The homogeneous mixtures of PAA partly neutralized by NaOH with C_{14}AB or PDADMAC with SDS have been studied by high-speed sedimentation technique in the range of Z where formation of insoluble PSCs is not observed ($Z \leq Z_c = 0.25$ for PA and $Z \leq Z_c = 0.4$ for PDADMAC). Figure 1 represents the sedimentation profiles of the studied homogeneous mixtures each revealing two peaks at $0 < Z < Z_c$, indicating that the both reaction mixtures contain the species of two different types.

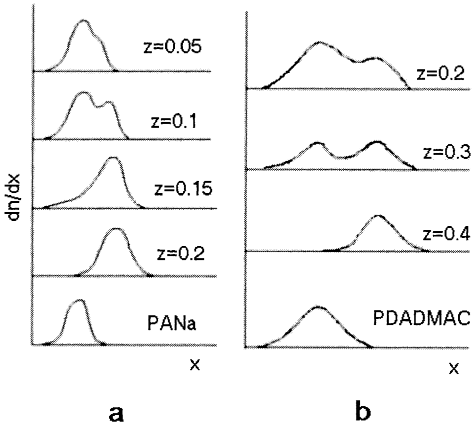

Figure 1. Sedimentation profiles for PA-C_{14}AB (a) and PDADMAC-SDS (b) mixtures.

Comparison of calculated sedimentation coefficients with those for the free PEs (Table 1) shows that the "slow" peaks correspond to the free polyions, while the "fast" - to the PSC particles. The increase of the surfactant concentration in both reaction mixtures is accompanied by decrease in the area of free PE peaks and increase in the area of the PSC peaks while the values of corresponding sedimentation coefficients are not changed (Figure 1 and Table 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) irrespectively of PE or S nature. 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 PEs and water-soluble PSCs of a constant composition, $\varphi = \varphi_c$. Therefore, we may conclude that the surfactant ions incorporated in such PSC species form micelles of the minimum size, i.e of the minimum aggregation number (n_{min}) characteristic for the investigated systems at the given experimental conditions.

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

PA-C_{14}AB			PDADMAC-SDS		
Z	**S_1x10^{13}, s**	**S_2x10^{13}, s**	**Z**	**S_1x10^{13}, s**	**S_2x10^{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

For evaluation of n_{min}, the values of M_w of PSCs were measured by static laser light scattering. The M_w of PA-C_{14}AB complex was determined from low angle light scattering data at $\theta=6.5^0$ using the Debye extrapolation. The double Zimm extrapolation was used in the case of PDADMAC-SDS PSCs (Figure 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 either association or dissociation of PSC species within the whole concentration range ($5x10^{-5}<c<3x10^{-4}$ g/ml). From the obtained M_w values, 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]. All these data are summarized in Table 2.

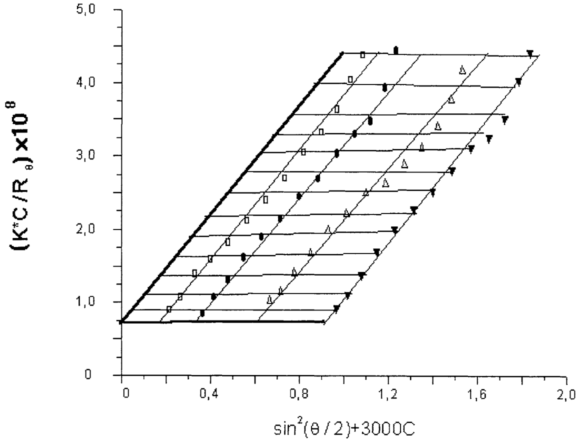

Figure 2. Zimm plot for PDADMAC-SDS system, C_{NaCl}=0.05M, Z=0.4.

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	-	5.0	1	-	2.1	10
PSC PA-C_{14}AB	0.25	8.3	0.9	130	4.6	5
PDADMAC	-	46	1	-	1.0	21
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, at $Z=Z_c$, contains only one PA chain and *ca.* 10^2 surfactant ions. It shows that PA-surfactant interaction is not accompanied by polyelectrolyte association. Hence, in this case PSC solutions may be considered as solution of individual complex macromolecules. The estimated n_{min} value is close to an aggregation number corresponding to spherical micelles which free C_{14}AB forms in water solutions[7]. It suggests that each complex species contains one spherical micelle bound to a single PA chain. In other words, *ca.* 100 S-ions are neutralized by the equal number of PA carboxylate groups while other 500 PA units are exposed to water environment providing solubility of the whole complex species. It is important that in the case of PA-C_{14}AB complex the polyanion does not change the morphology of the micellar phase characteristic for the free surfactant above its cmc.

Entirely different situation has been observed for PDADMAC-SDS PSCs. The M_w of PSC species drastically exceeds M_w of free PDADMAC indicating aggregation of the PE chains. Moreover, the estimated n_{min} value by 3 order of magnitude exceeds n_{min} characteristic for free SDS spherical micelles. Hence, in this case, the PE imposes another morphology, not typical for the micelles of the free surfactant. Figure 3 shows the patterns of distributions by diffusion coefficients for free PDADMAC and its mixtures with SDS at different Z values recovered from the autocorrelation functions of scattered light. As is seen, free PDADMAC is characterized by unimodal distribution function, diffusion coefficient corresponding to the distribution maximum being $D_{z1}=10^{-7}sm^2/s$. Addition of small amounts of SDS into PDADMAC solution results in appearance of the second diffusion mode characterized by $D_{z2}=10^{-8}sm^2/s$ at a maximum indicating formation of the PSC species with the average hydrodynamic radius R_e *ca.* 100nm. This value is approximately five times higher than R_e of the free polycation (*ca.* 20nm). Increase of SDS content in the reaction mixture up to Z=0.4 leads to linear increase of the average light scattering intensity accompanied by an enlargement of PSC distribution mode (and consequently, increase of the contribution of PSC species into the overall scattering), the maximum of the modes being invariable. It means that in the whole range of Z studied, increase of SDS content results in an increase of the number of PSC species with the constant molecular characteristics (D_z and M_w). Hence, the PSC composition remains unaltered (φ_c=0.4) correlating with the aforementioned constancy of the sedimentation coefficient.

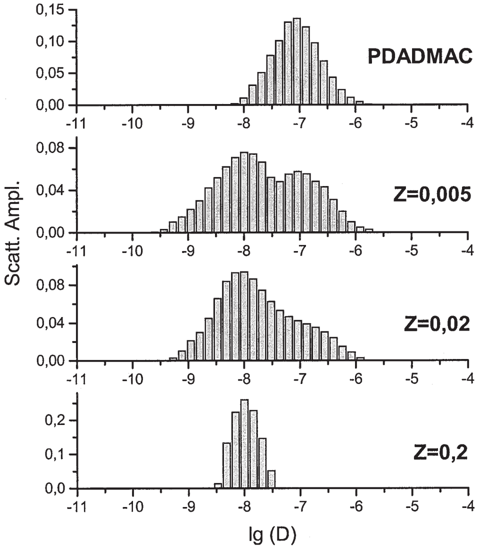

Figure 3. Distributions by diffusion coefficients for PDADMAC and its complexes with SDS. [PDADMAC]=1.1×10^{-2}M, c_{NaCl}=0.05M.

The question of morphology of SDS species formed by PDADMAC and SDS which coexist with the free polycations at $Z<Z_c$ preserving their integrity is of a major importance. One may assume that such species represent vesicles formed by the SDS bilayer which outer and inner leaflets are neutralized by adsorbed PDADMAC units while the excess PE segments are exposed to outer and inner water environment. Formation of such vesicles involving a part of the total number of PE chains may be favorable in dilute solution, because of the contribution of free PE chains in translational entropy. Figure 4 represents a hypothetical scheme of SDS – PDADMAC vesicle, where d is the thickness of bilayer and R is the distance from a vesicle center to the external surface of bilayer. On the base of the measured number of SDS ions in PSC micelle: $\overline{n}_{surf}$= $n_{min}=1.5\times10^5$; and known molar mass of alkyl group in SDS: M_{DS}=265g/mol; density of hydrocarbon micelle core formed by SDS alkyl groups: $\rho_{DS}=0.8$ g/cm^3=8×10^{-22} g/nm^3 and a thickness of bilayer equal to doubled alkyl group length: d=3 nm, it is possible to calculate the surface area per one surfactant ion.

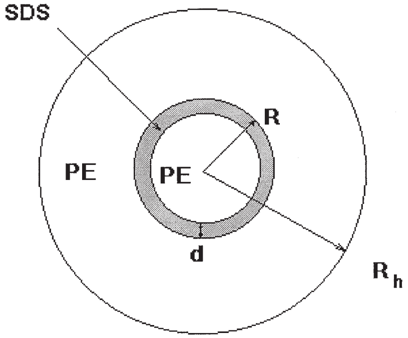

Figure 4. Hypothetical scheme of SDS – PDADMAC vesicle.

The volume of spherical bilayer in hypothetical vesicle:

$$V_{DS}=\frac{4}{3}\pi[R^3-(R-d)^3 \quad (1)$$

should be equal to the total surfactant volume:

$$V_{DS}=\frac{m}{\rho_{DS}}=8.3\times10^4\,\mathrm{nm}^3 \quad (2)$$

Solution of equations (1) and (2) gives R=49nm.

Then, the surface area per one SDS ion is:

$$S_{calc}=\frac{4\pi\left[R^2+(R-d)^2\right]}{n_{surf}}=0.38n$$

that satisfactorily agrees with the value known from the literature (S=0.32 nm^2 [8]). In fact, the proposed vesicle structure of PDADMAC-SDS PSC was confirmed by electron microscopy that will be published elsewhere in details.

The above data show that PDADMAC in contrast to PA drastically changes the morphology of intracomplex micellar phase formed by oppositely charged S-ions comparing to its morphology in the free state.

The change in the concentration regime of PDADMAC solution crucially affects the structure and the phase state of PDADMAC-SDS system at fixed $Z<Z_c$. It was shown earlier that solutions of PDADMAC of Mw=$4.6\text{x}10^5$ at concentrations lower than $3\text{x}10^{-2}$ base mol/l should be considered as diluted, while at concentration range from $3\text{x}10^{-2}$ to $9\text{x}10^{-2}$ base mol/l transition from diluted to semidiluted regime is observed (crossover region)[4,9].

Figure 5 shows that addition of SDS to dilute PDADMAC solution causes only slight change in the solutions viscosity, while at the concentration of PDADMAC above 3x10^{-2} base mol/l sharp increase of viscosity accompanied by gelation of the system is observed.

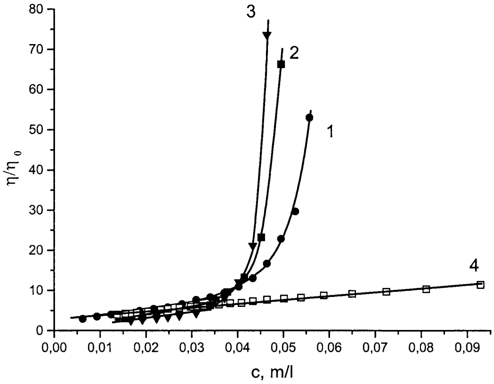

Figure 5. Viscosity of PDADMAC-SDS complexes *vs*. PDADMAC concentration at Z=0.2 (1), 0.3 (2) and 0.4 (3) and that for PDADMAC (4), 20°C.

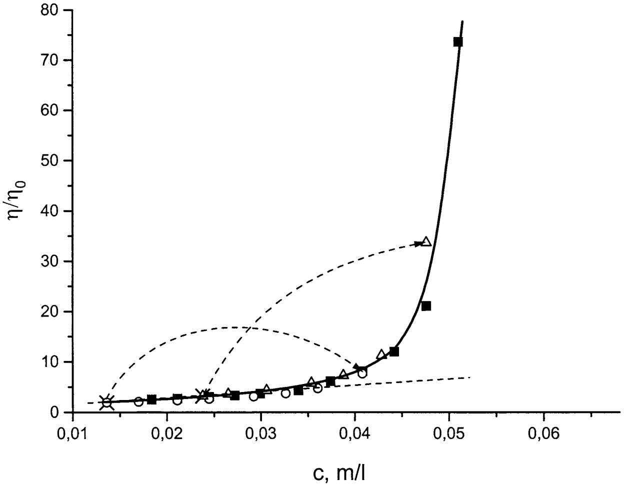

Figure 6. Viscosity of PDADMAC-SDS complexes solutions *vs*. PDADMAC concentration at Z=0.4. Dark squares correspond to direct mixing of the components; arrows show the viscosity change on concentrating of initial solutions marked with crosses by evaporation of water; light dots and triangles correspond to consecutive dilution of the system with water after evaporation.

The formation of stable homogeneous gels occurs in all range of Z studied ($0<Z\leq0.4$). It is significant that for all $Z\leq Z_c$, gelation starts at the same PDADMAC concentration

corresponding to the crossover region for free polymer solution[4,9]. Remarkably that the gelation process is fully reversible. It follows from the data of Figure 6 representing the plots of viscosity *vs.* PDADMAC concentration on diluting and concentrating at fixed Z. The values of viscosity of the systems prepared either by direct mixing of the components, or by dilution of a more concentrated solution with water, or by evaporation of water from the less concentrated solutions actually coincide.

The transformation of vesicle PSC species into gel upon change of the concentration regime of PDADMAC solution is probably caused by loosing of the entropy benefit due to elimination of translational degrees of freedom of PDADMAC chains. As the result, non-uniform distribution of S-ions transforms to a homogeneous distribution.

Conclusion

The above studies demonstrate that either the chemical nature of the polyelectrolyte or concentration regime of PE solution control size and structure of PSC in solutions. In fact, in the case of PA-C_{14}AB complexes n_{min} of the surfactant ions within PSC micelles is close to that in the polymer-free surfactant solutions indicating formation of intercomplex spherical micelles. On the contrary, in the case of PDADMAC-SDS complexes the n_{min} value is at least three orders of magnitude higher than that for free SDS indicating formation of a micellar phase with absolutely different morphology most likely vesicles. Moreover, a shift from dilute to semidilute regime in PDADMAC solution leads to formation of reversible PSC gels.

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