Binding of Carboxy-Terminated Anionic/Nonionic Mixed Micelles to a Strong Polycation: Critical Conditions for Complex Formation[†]

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Mixed micelles of carboxy-terminated surfactants and nonionic surfactants bind to the polycation PDADMAC at a well-defined critical pH corresponding to a critical micelle surface charge density σ_c. The ionic strength dependence of σ_c for this and a number of related polyelectrolyte–micelle systems conforms to the simple result $\sigma_c = A\kappa^{1.4}$, where κ is the Debye–Hückel parameter and A varies inversely with polymer linear charge density. The interdependence of σ_c and κ also leads to the observation that binding occurs when the potential due to the micelle exceeds −9 mV at a distance of 8 Å from the micelle surface.

Introduction

The interactions between colloidal particles and polyelectrolytes of opposite charge are relevant to a number of problems in colloid dispersions[1] and in biochemistry. Two groups of theoretical treatments have developed around this question, in the context of these two fields. The first derives from investigations of the interaction of flexible chain polyelectrolytes with oppositely charged planar or curved surfaces.[2-6] While the models and approaches applied in these studies differ considerably in detail, all these treatments lead to the observation of phase-transition-like behavior, i.e., the appearance of a bound polymer state at certain critical conditions. These treatments are often expressed[2] in terms of a critical temperature, but since the effects of temperature on, e.g., the release of bound counterions, ion hydration, and water structure are typically disregarded, it is reasonable to consider the isothermal form of the final results, namely

$$\sigma_{crit}\xi \sim \kappa^b \tag{1}$$

where σ is the surface charge density of the colloid plane, ξ is the linear charge density of the polyelectrolyte, κ is the Debye–Hückel parameter, and the scaling term b differs in the various treatments, being 3, 11/5, and 1, in references 2, 3, and 4, respectively. Treating the case of spherical surfaces, Muthukumar found little change relative to the situation for planar surfaces.[6] A second and very different approach derives from studies of interactions between DNA and proteins or peptides, particularly the strongly basic (positively charged) DNA-binding proteins and polypeptides, such as nucleohistones and spermine or oligolysines, respectively. Since DNA

(persistence length ca. 50 nm) approximates a rigid rod in the length scale of typical protein dimensions, chain flexibility is neglected, and theories for this phenomenon treat the protein or oligopeptide as a large multivalent ligand which displaces some well-defined number of counterions from the DNA rod.[7-9] Consequently, the influence of the ionic strength appears in a form very different from eq 1, i.e.

$$K_b \sim (I)^{z_2/z_1} \tag{2}$$

where K_b is the protein- or peptide-DNA binding constant, z_1 is the valence of DNA's counterion, and z_2 is the number of counterions displaced upon binding, related to the number of ligand charge sites involved in the binding process.

Unambiguous experimental verification of either expression 1 or 2 is difficult. With regard to experimental tests of eq 2, there appears to be considerable evidence to support a logarithmic dependence on the ionic strength for the binding constant of DNA–protein systems, but z_2 is, to a large extent, a fitting parameter, as the number of ions displaced upon protein binding is difficult to predict a priori from protein structure. With regard to eq 1, there have been relatively few observations of the predicted transition behavior.

Observations of a well-defined point of incipient complex formation have been reported by us for several systems involving strong polyelectrolytes and oppositely charged micelles,[10-13] proteins,[14] or dendrimers.[15] However, comparisons with eq 1 are complicated by several factors. In protein–polyelectrolyte systems, the surface charge heterogeneity of the former has an important effect, presum-

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ably accounting for the binding of polyelectrolytes to proteins on "the wrong side of the isoelectric point".[16] For most of the micelle systems investigated, the surface charge density was adjusted by using mixtures of ionic surfactants (particularly sodium dodecyl sulfate) and nonionic surfactants with long polar headgroups, i.e., ethylene oxide chains. The location of the ionic headgroup within the "palisade layer" of the nonionic headgroups, makes it difficult to envision the "surface" to which the polyelectrolyte binds.[17]

In the present study, we employ micelles based on a new class of surfactants, carboxy-terminated alkyloxy-ethylenes[18] (CAE). In CAE micelles, the ionophores must be located in the outer surface region of the colloid particle. From their titration curves, one may determine the dependence of pK_a on the degree of dissociation, α, and then the micelle surface potential ψ_0 as a function of pH. If the micelles are spherical, application of the Poisson–Boltzmann equation in spherical geometry allows one to calculate micelle surface charge density, σ. This measurement of σ is much more reliable than attempts to find σ from α and geometric considerations, since the influence of counterion binding is automatically taken into account, inasmuch as that factor will suppress ψ_0. Control of micelle surface potential and geometry may additionally be achieved by the formation of mixed micelles of CAE and $C_{12}E_n$ nonionic surfactants. The use of such mixed micelles enables us to (1) control mixed micelle size and (2) reduce σ to the desired magnitude while maintaining α in the range where precise determination of α by potentiometry is facilitated.

Total intensity and dynamic light scattering (DLS) measurements were used to identify the pH of incipient complex formation between CAE micelles and poly-(dimethyldiallylammonium chloride) (PDADMAC), as a function of NaCl concentration. PDADMAC is a strong (i.e., pH independent) polycation of moderate charge density (about 0.65 nm between charges) and chain stiffness (persistence length about 3 nm in 0.1 M NaCl). Upon adjustment of pH, the terminal carboxylic acid groups of the CAE micelles become ionized. When the micelle surface charge density attains a critical value, an increase in scattering signals the formation of a poly-electrolyte–micelle complex. We then find the dependence of σ_c on κ, which may be used to test the validity of eq 1.

Experimental Section

Materials. Poly(diallydimethylammonium chloride) (PDAD-MAC), $M_n = 1.5 \times 10^5$, was obtained from Dr. W. Jaeger, Fraunhofer Institut (Teltow, Germany). The carboxy-terminated alkyloxyethylene (CAE) surfactant, sodium dodecyl hexaethoxy-carboxylate $C_{12}H_{25}(OCH_2CH_2)_6OCH_2COONa$ ($C_{12}E_6C_2Na$), was from Lion Corp. (Tokyo), with a purity >98%. The monodisperse nonionic surfactant octaoxyethylene glycol *n*-dodecyl ether CH_3-$(CH_2)_{11}(OCH_2CH_2)_8OH$ ($C_{12}E_8$) was from Nikko Chem. Co. (Tokyo). Milli-Q-water was used throughout the work.

Turbidity, Total Intensity, and Dynamic Light Scattering. Preliminary "type 1" titrations were carried out by titration of mixed anionic/nonionic surfactant micelles with NaOH in the presence of PDADMAC, at fixed ionic strengths ranging from 0.02 to 0.20 M NaCl. The transmittance was monitored as a function of pH with a Brinkmann P800 probe colorimeter. To more precisely determine pH_c, corresponding to the onset of polymer–micelle complexation, aliquots from the type 1 titration were removed for DLS measurements, which were carried out on solutions containing 0.6 g/L polymer, and nonionic/anionic

surfactant mixtures (total surfactant concentration 8 mM). A DynaPro 801 (Protein Solutions Inc., Charlottesville, VA), which employs a 30 mW solid-state 780-nm laser and an avalanche photodiode detector, was used to determine both apparent Stokes radii (R_s^{app}) (via the method of cummulants) and 90° total scattering intensities (I_S). Size distributions were further studied by DLS using a Brookhaven Instruments system equipped with a 72-channel digital correlator (BI-2030AT) and an OmNichrome air-cooled 200 mW argon ion laser operating at 488 nm. The data, obtained on solutions containing 0.6 g/L polymer and 3:1 nonionic/anionic surfactant (total concentration 16 mM), were analyzed using CONTIN. It is important to note that the critical micelle concentration (cmc) reported for $C_{12}E_8$ is 0.08 mM[19] and, furthermore, that the addition of anionic surfactant at low concentrations to nonionic surfactant generally depresses the cmc. Thus all experiments are conducted at surfactant concentrations at least 2 orders of magnitude above the cmc, so that the role of a nonmicellar surfactant can be safely ignored.

pH Titrations. To establish the relationship between pH and the degree of ionization α of CAE, pH titrations of (polymer-free) mixed micelle solutions (total surfactant 40 mM) were conducted using a Beckman 34 pH meter equipped with a Beckman combination electrode (39848), under nitrogen atmosphere with moderate stirring. All experiments were carried out at 24 ± 1 °C.

Results

For mixtures of CAE micelles and PDADMAC at ionic strengths from 0.10 to 0.35 M, scattering intensities were found to diminish with pH, and sometimes displayed a maximum. This complex behavior was found to arise from the growth of micelle size at low pH: as the degree of ionization of CAE diminishes from 0.2 to 0, the value of R_s^{app} increases from 3 to 10 ± 2 nm (depending upon ionic strength), with a concomitant increase in scattering intensity. This micelle growth is presumably due to the small effective size of uncharged CAE headgroups and may or may not involve intramicellar hydrogen bonding but, in any event, obscures complex formation. Micelle growth was slightly diminished when CAE was mixed with equimolar $C_{12}E_6$, but micellar mixtures of CAE and $C_{12}E_8$ (1:2 or 1:3) remained spherical with $R_s^{app} = 3$ nm at all pH, and therefore the dependence of I_S on pH for polymer-free micelles was small. For this reason, we elected to carry out experiments using 1:3 CAE/$C_{12}E_8$ and determined the critical pH at which this spherical mixed micelle just begins to bind to PDADMAC. To further enhance detection of the critical pH, the scattering intensity of the polymer-free system was subtracted from that of the polymer-containing system so that this ΔI_S would represent the enhancement of scattering due to complex formation.

The dependence of ΔI_S on pH is shown in Figure 1 for 1:3 $C_{12}E_6C_2Na/C_{12}E_8$ (total surfactant concentration 8 mM) in the presence of 0.6 g/L PDADMAC, at ionic strengths ranging from 20 to 200 mM NaCl. As in other polyelectrolyte–micelle systems studied,[10–12] the onset of complexation is signaled by an increase in scattering intensity at pH_c. However, in contrast to systems such as PDADMAC/SDS–Triton X-100, the increase in I_S is modest. Despite increasing micelle charge, no further increase in scattering is observed when pH exceeds pH_c by more than 0.4 pH unit, for $I > 0.15$ M. Furthermore, phase separation cannot be induced for $I > 0.10$ M regardless of pH, a situation distinct from studies with other polyelectrolyte–micelle systems, wherein an increase in micelle charge density always leads to either coacervation or precipitation.[11,12,20]

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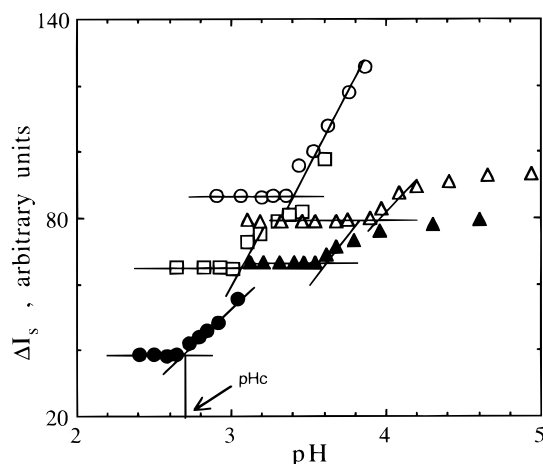
Figure 1. 90° scattering intensity (arbitrary units) for $C_{12}E_6C_2$-Na (2 mM)/$C_{12}E_8$ (6 mM) + PDADMAC (0.6 g/L) corrected by subtraction of polymer-free blank, at different ionic strengths (M): 0.02 (●); 0.06 (□); 0.10 (○); 0.15 (▲); 0.20 (△). Curves offset for clarity. pH_c shown for 0.02 M NaCl.

Apparent size distributions were obtained via DLS using CONTIN, as shown in Figure 2 for $I = 0.02$ M (a) and for $I = 0.15$ M (b). In the former case, distributions are constant for pH < 2.7 but subsequently broaden and become bimodal with further increase of pH. These results confirm the identification of $pH_c = 2.7$ at $I = 0.02$ M via Figure 1. The same pattern in Figure 2b verifies the more problematic identification of $pH_c = 3.6$ for $I = 0.15$ M.

The surface potential at critical conditions was determined from pH titration data, which are presented as $pK_a = pH + \log(1 - \alpha/\alpha)$ vs α in Figure 3. The difference between pK_a and pK_0 at any α leads to the surface potential ψ_0 (at the site where H^+ originates) via eq 3

$$pK_a - pK_0 = 0.434e\psi_0(\alpha) \tag{3}$$

Since the measured surface potentials are typically less than 25 mV, the relationship between σ_c and $(\psi_0)_c$ for spherical micelles of radius a is obtained through the Debye–Hückel approximation as

$$\sigma_c = \epsilon_0\epsilon_r(\psi_0)_c/4\pi[(1 + \kappa a)/a] \tag{4}$$

where ϵ_0 and ϵ_r are the dielectric constant and permittivity of a vacuum, respectively, and κ is the Debye–Hückel parameter. The values of the surface charge density at α_c corresponding to pH_c for the different ionic strengths are given in Table 1.

Discussion

The data in Table 1, presented as a plot of σ_c (given for convenience as esu cm^{-2} (1 C m^{-2} = 3 × 10^5 esu cm^{-2})) vs ionic strength, can be considered a phase boundary that defines conditions for complex formation in terms of micelle surface charge density and ionic strength. In view of eq 1, it is also useful to plot the dependence of σ_c on κ, or more conveniently, on $\kappa' = I^{1/2} = 0.304\kappa$, where the units of κ are nm^{-1}. Given the general form of eq 1, we made b a fitting parameter and obtained a correlation of $r^2 = 0.997$ for $\log \sigma_c = \text{constant} + b \log \kappa'$, with $b = 1.4$. To generalize this behavior, we also plotted σ_c vs κ' for another system in which spherical micelles complex with strong polyelectrolytes, namely, micelles of dimethyldodecylamine

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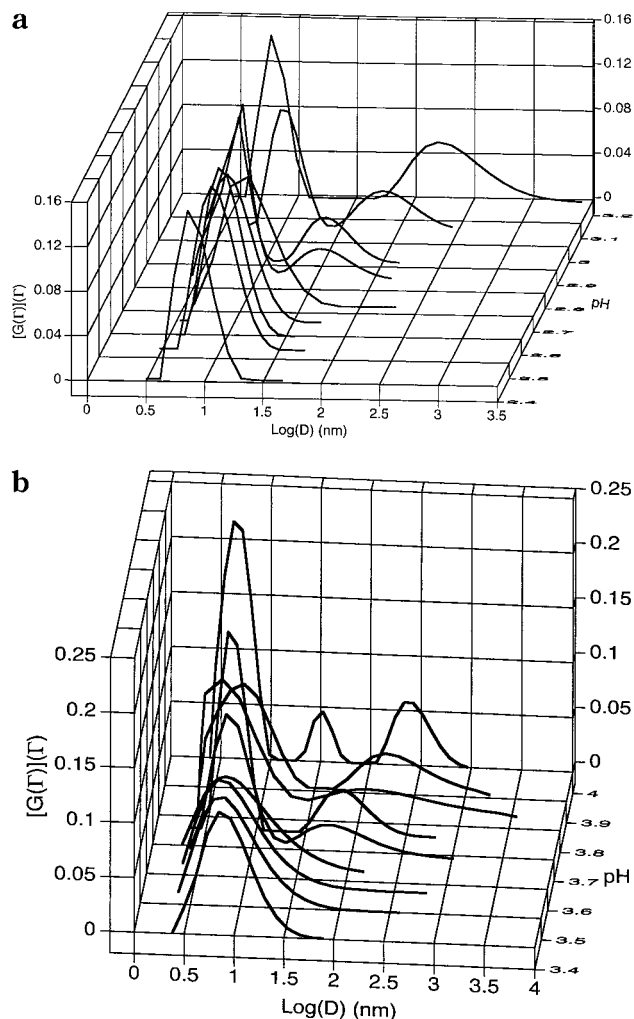
Figure 2. Distribution of apparent hydrodynamic diameters for $C_{12}E_6C_2Na/C_{12}E_8$ (4 mM/12 mM) + PDADMAC (0.6 g/L) system at (a) $I = 0.02$ M (2.4 < pH < 3.2), and (b) $I = 0.15$ M (3.4 < pH < 4.0). (The peaks on the left are identified as free micelles).
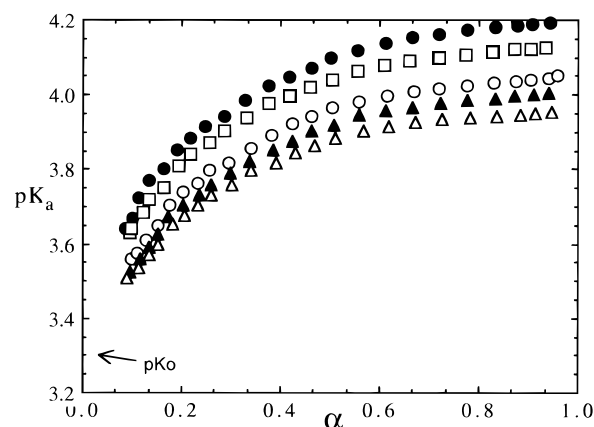

Figure 3. pK_a vs α for mixed $C_{12}E_6C_2Na/C_{12}E_8$ micelles (10 mM/30 mM) at ionic strengths (M): 0.02 (●); 0.06 (□); 0.10 (○); 0.15 (▲); 0.20 (△).

oxide (DMDAO) interacting with strong polyanions,[21] and found similar behavior. These results are summarized in Figure 4, which presents phase boundaries as the dependence of $|\sigma_c|$ on $(\kappa')^{1.4}$ for PDADMAC–CAE/$C_{12}E_8$ along with the systems from ref 20: DMDAO micelles with (a)

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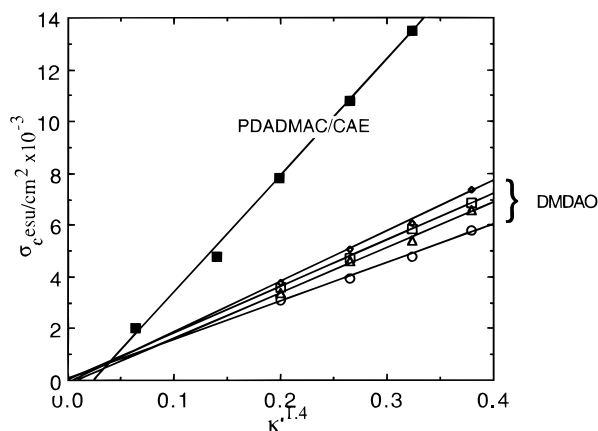
Figure 4. Ionic strength dependence of the critical micelle surface charge density, plotted as σ_c vs $(\kappa')^{1.4}$ where $\kappa' = I^{1/2}$. From top to bottom: CAE/C12E6-PDADMAC (this work); DMDAO−81% sulfonated NaPSS, DMDAO−NVP/AMPS (36:64) copolymer, DMDAO−NaPSS, DMDAO−NaPAMPS (all from ref 13).

Table 1. Ionic-strength Dependence of CAE-$C_{12}E_8$ Micelle Surface Charge Density at critical condition for binding to PDADMAC

| I, M	σ_c, C m^{-2}	I, M	σ_c, C m^{-2}
0.02	−0.0071	0.15	−0.034
0.06	−0.017	0.20	−0.044
0.10	−0.025		

sodium poly(styrenesulfonate) (NaPSS); (b) 81% sulfonated NaPSS; (c) sodium poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS); (d) the copolymer of *N*-vinypyrrolidone (NVP) and NaAMPS (36:64 NVP/AMPS).

Although the exponent 1.4 arises as a fitting parameter, it is worth noting the quality of the fit, with the average regression coefficient for Figure 4 being $r^2 = 0.998$, and the poorest fit $r^2 = 0.990$. It is also noteworthy that the results suggest a limiting value as I approaches 0 of $\sigma_c = 0$. In accord with eq 1 the slope is seen to vary inversely with ξ; i.e., NaPSS and NaAMPS display the smallest slope, 81% NaPSS and 64% PAMPS exhibit slightly larger slopes, and PDADMAC, with the largest spacing between ionophores and thus the lowest value of ξ, showing largest κ dependence. While the exponent 1.4 is not in agreement with any of the theoretical results represented by eq 1, it is important to point out that those treatments are for surfaces of low curvature.

Since the surface potential of the CAE/$C_{12}E_8$ micelles at critical conditions is known, we can calculate the potential decay curve at each ionic strength according to

$$\psi(x) = \psi_0(a/r)\exp[-\kappa x] \qquad (5)$$

where $x = r - a$ is the distance from the micelle surface (here defined as the locus of carboxylic acid groups). Figure 5 displays the potential decay curves for ionic strengths 0.06, 0.10, 0.15, and 0.20 M. The calculation was not performed at $I = 0.02$ M because estimating the contribution of polycation and micelle to the ionic strength becomes problematic at low I. The plot of Figure 5, expanded in the range of ca. 10 mV, reveals a common intersection at $x \cong 8$ Å and a potential close to −9 mV. Thus, binding to PDADMAC occurs when the absolute value of the potential at a distance of 8 Å from the micelle surface exceeds 9 mV. Similar behavior was observed for the systems involving DMDAO micelles in ref 20, with a common intersection at $x^* = 6$ Å and $\psi^* = +5$ mV.
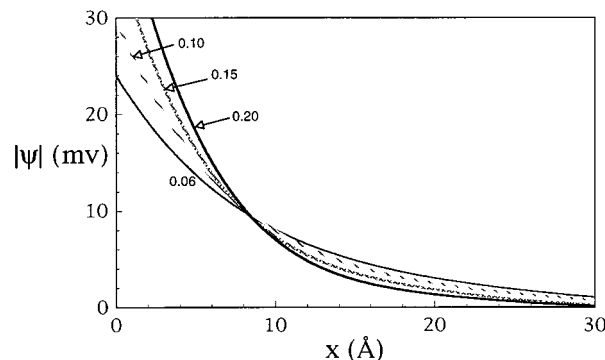
Figure 5. Potential vs distance (x) from micelle surface at critical conditions for complex formation between $C_{12}E_6C_2Na$/$C_{12}E_8$ micelles and PDADMAC, at ionic strengths (M) shown.

A reasonable interpretation of the above results is that the common point (x^*, ψ^*) reflects the mean locus of bound polymer segments. While the polymer segments in the bound state clearly occupy a range of positions, the finding that x^* is smaller for DMDAO micelles with polyanions than for CAE/$C_{12}E_8$ micelles with PDADMAC can reflect either the more diffuse surface of the CAE/$C_{12}E_8$ micelles or the greater stiffness of PDADMAC, both of which would lead to less intimate contact between bound polyion residues and micelle surface. As a rather severe simplification we can hypothesize a point charge z equivalent to the cooperatively bound sequence of polyion residues, such that the energy required to separate polyion and micelle at some pH and I is equal to the energy of removing a charge z from the bound position at x^*. If we set this energy at critical conditions equal to kT (where $kT/e = 25.7$ mV), we obtain the value of $z = 25.7/\psi(x^*)$. While values of z/e were found to be 5.5 for DMDAO micelles with NaPAMPS and 4.6 for DMDAO micelles and NVP/AMPS,[20] we obtain $z/e \approx 3$ for PDADMAC−CAE/$C_{12}E_8$. The decrease in z/e from NaPAMPS to NVP/AMPS to PDADMAC corresponds to a decrease in ξ. The interpretation of these results is that the number of adjoining polyion segments that forms a cooperative binding unit upon complexation with a spherical micelle of radius r is geometrically constrained to a certain contour length (perhaps on the order of r). Consequently, the value of z/e decreases with diminishing polymer charge density. Since binding occurs when $\psi(x^*)z = 25.7$ mV, we can explain why the potential at the intersection point increases with decreasing ξ, e.g., 5 mV for NaPAMPS vs 9 mV for PDADMAC.

It is also of interest to compare critical pH values and surface charge densities found here to comparable micelle charge parameters for the system containing mixed micelles of Triton X-100 (TX100) and sodium dodecyl sulfate (SDS),[22] also with PDADMAC. The micelle surface charge density σ in that case is controlled by the mole fraction of anionic surfactant, i.e., $Y = [SDS]/\{[SDS] + [TX100]\}$, so that Y is the fraction of surfactant headgroups that bear a charge. For ionic strengths $I = 0.10$ and 0.20, we found $Y_c = 0.09$ and 0.15, respectively. In the present system, the fraction of surfactant headgroups that bears a charge at critical conditions is $\alpha_c f$, where $f = 0.25$ is the mole fraction of CAE. For $I = 0.01$ and 0.20, we find $\alpha_c f = 0.09$ and 0.14. These results indicate that the critical micelle surface charge densities at $I = 0.01$ and 0.02 M for the system PDADMAC−SDS/TX100 are very similar to those for the present system PDADMAC−CAE/$C_{12}E_8$.

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However, one striking difference is the lack of an substantial increase in turbidity upon further increase in σ for the latter. We attribute this to two causes. First, in the present case, the mole fraction of charged surfactant does not exceed 0.25 even at high pH, whereas phase separation for PDADMAC−SDS/TX100 generally requires Y_c in excess of 0.35. Second, we note from Figure 3 that the increase in micelle surface potential, as manifest in $pK_a - pK_0$, increases very slowly with α above $\alpha = 0.5$. This is particularly striking for the highest ionic strength, $I = 0.20$, where pK_a becomes virtually constant for $\alpha \geq 0.7$. We believe that the suppression of micelle potential in this case is due to specific binding of Na^+ ions to COO^-. Similar effects have been observed for carboxyl-terminated dendrimers,[23] in which case colloid surface potentials were found to increase when the supporting electrolyte counterion was changed from Na^+ to TMA^+, and for the binding of cationic micelles to polyanions,[24] in which case the effective micelle binding affinity of poly(acrylic acid) is diminished by Na^+ much more than by TMA^+.

Finally, a brief comment on the apparent size distributions of Figure 2 may be appropriate. In Figure 2a, the first new mode that appears upon increase of pH exhibits an apparent hydrodynamic diameter close of 30 nm, close to that of polymer alone, so it is reasonable to attribute this to an intrapolymer complex. Higher-order aggregation of this primary complex, previously identified for similar complexes between PDADMAC and SDS/Triton X-100

micelles,[25] presumably leads to the slower diffusivity modes at higher pH with apparent diameters greater than 200 nm. When the size of the higher-order aggregate is sufficiently large, it may be possible for it to be resolved by CONTIN from the primary complex: this appears to be the case at pH 4 and $I = 0.15$ M as shown in Figure 2b.

Conclusions

The binding of either polycations to spherical anionic micelles or polyanions to spherical cationic micelles follows a simple empirical relationship: the micelle surface charge density σ at critical binding conditions depends on the ionic strength to the 0.7 power, with a proportionality constant that varies inversely with the polymer linear charge density. A second characteristic feature of such systems is that potential decay curves constructed by assuming a screened Coulombic potential around the micelle exhibit a common intersection for values of σ and I corresponding to critical conditions. The implication of this finding is that binding takes place when the potential exceeds some well-defined value at a particular distance from the micelle surface and that this distance must be related to some mean position of the bound polymer segments.

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