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Effect of EO Chain Length of Dodecanol Ethoxylates ($C_{12}E_n$) on the Complexation of $C_{12}E_n$/SDS Mixed Micelles with an Oppositely Charged Polyelectrolyte

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Turbidimetry, dynamic light scattering, and capillary electrophoresis were used to study the complexation of polydiallyldimethylammonium chloride (PDADMAC) with mixed micelles of sodium dodecyl sulfate (SDS) and dodecanol ethoxylates ($C_{12}E_n$). The effect of EO chain length and its distribution was examined using various combinations of $C_{12}E_n$ ($n = 4, 6, 8, 12$). The results show that the onset of the complexation of PDADMAC with the mixed micelles is affected by the EO chain length of $C_{12}E_n$: the mole fraction (Y) of SDS in the mixed micelle required to form the complex (Y_c) increases with n. The effect of EO chain length on the onset of bulk phase separation shows the same trend. Although Y_c varies with n, the electrophoretic mobility of mixed micelles with composition corresponding to Y_c is independent of n. We propose that the effect of EO chain length has two aspects: (1) an increase in the average distance between bound polycation segments and the SDS sulfate groups, and (2) an increase in the distance between SDS head groups, which causes a decrease in the surface charge density (σ) of the micelle. Therefore, the electrical potential at the mean locus of bound polymer segments, ψ_0, decreases with increasing n; in order for complexation to occur, this effect must be compensated for by a larger value of Y. Broader distributions of EO chain length lead to an increase in the range of Y over which the soluble complex is stable. We suggest that polycations initially bind to micelles which are rich in shorter EO chains and thus have higher "surface" potential, ψ_0. However, additional SDS may go preferentially into micelles rich in longer chains with lower ψ_0. This delays the formation of micelles which have sufficiently large ψ_0 to cause phase separation. © 1996 Academic Press, Inc.

INTRODUCTION

Studies of complexation between charged micelles and oppositely charged polyelectrolytes have shown that electrostatic interaction is the dominant force for complexation (1–3). The surface charge density of micelle, σ, is therefore a particularly important variable, which may be conveniently controlled by adjusting the mole fraction (Y) of the ionic component in mixed micelles. Upon increasing Y, one observes a transitional point (Y_c) corresponding to the onset of polyelectrolyte binding followed by bulk phase separation with further increase of Y (Y_p). Many polyelectrolyte–mixed micelle systems have been studied in this manner by monitoring the dependence of the turbidity or mean particle size on Y (4, 5). Some of these include mixtures of dodecanol hexaoxyethylene ether ($C_{12}E_6$) with sodium dodecyl sulfate (SDS), or TX-100 with SDS, in combination with polycations such as polydiallyldimethylammonium chloride (PDADMAC), polymethacrylamidopropyltrimethylammonium chloride (PMAPTAC), etc. (5); or mixed positively charged mixed micelles, such as TX-100/dodecyl trimethylammonium bromide (DTMAB) in combination with polyanions, such as sodium polystyrene sulfonate and sodium polyvinyl sulfate (NaPVS) (3).

There is substantial evidence to show that the significant interaction is between polyelectrolyte and mixed micelle, not between polyelectrolyte and ionic monomeric surfactant. (i) There is no effect of the concentration of anionic surfactant per se: no complexation is observed, regardless of anionic surfactant concentration, as long as nonionic surfactant is in suitable excess. (ii) Many studies (1–3) have shown that complex formation occurs only when some critical micelle surface charge density is attained, an unlikely scenario if complex formation involved nonmicellar surfactant. (iii) The mixed micelle cmc is typically on the order of 0.1 mM, i.e., 2 orders of magnitude smaller than the surfactant concentration, so micelles are abundant relative to monomer. It is interesting to note that this effect, the depression of the cmc upon addition of nonionic surfactant (by well over an order of magnitude for, e.g., SDS/TX-100) may be responsible for the relatively low tendency of anionic surfactants in the presence of nonionic detergents to denature proteins or delipidate biological membranes.

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Earlier studies (3, 6) have led to an empirical relationship that describes the critical conditions for complexation (6):

$$\sigma_c \xi \kappa^{-1} = \text{Constant}. \qquad [1]$$

This expression relates the charge density of the micellar surface at incipient complex formation σ_c to the Debye length, κ^{-1}, and the linear charge density of the polyion (the number of charges per unit contour length), ξ. This relation is similar in form to results of theoretical treatments for the interaction of polyions with oppositely charged surfaces (7–9), all of which predict that the bound state of the polyion appears at some critical surface charge density, σ_c, which varies inversely with ξ and κ^{-1}. Therefore, observations of Y_c can in principle be used to test theories that predict the value of σ at the onset of polyelectrolyte adsorption (7–9). However, although σ must depend directly on Y, its exact value may be ambiguous, particularly for micelles without well-defined surfaces.

Given the complexity of these systems, Eq. [1] is a remarkably simple result. However, this relationship only describes conditions for incipient complex formation. The detailed behavior of the system at $\sigma > \sigma_c$, i.e., in the region of soluble complexes and coacervation, shows a complex dependence on variables such as polymer MW (10, 11), polymer concentration (11–13), surfactant concentration (12), temperature (13), and structural features of the surfactants (2). For example, PDADMAC and SDS/TX100 form soluble complexes over a wide range of surfactant compositions (e.g., $0.23 < Y < 0.42$ in 0.4 *M* NaCl) while substitution of $C_{12}E_6$ for TX-100 virtually eliminates soluble complex formation, with coacervation occurring instead very near Y_c (2). It is of interest to examine the influence of the structure of the hydrophilic outer region of the micelle on its interaction with a strong polyion; similar effects may arise when highly charged biopolymers interact with cell membranes which also present to the polyion a surface composed of lipid head groups of varying charge and steric features.

The effect of the mole fraction of ionic component on polyelectrolyte-micelle interaction is obvious, but other factors such as counterion binding and the nature of ionic and nonionic head groups, have been less studied. In particular, the effect of the polyethylene oxide (EO) chain length in mixed micelles containing alcohol polyethoxylates has received little attention. Since EO chains may be large and flexible, they are likely to affect mixed micelle surface charge density by sterically separating and screening charged groups. Previous comparisons of SDS/$C_{12}E_6$ + PDADMAC and SDS/TX-100 + PDADMAC systems showed an influence of nonionic surfactant head groups on both Y_c and also the shape of the turbidity curve ([100 − *T*%] vs *Y*) (13). The current work systematically examines the effect of EO chain length on the complexation between $C_{12}E_n$/SDS micelles and PDADMAC, using turbidimetry, capillary electrophoresis (CE) and quasielastic light scattering (QELS).

EXPERIMENTAL

Materials. Polydiallyldimethylammonium chloride (PDADMAC), ‘‘Merquat 100’’ (Calgon corporation, Pittsburgh, PA), was dialyzed (nominal 10K ‘‘cutoff’’) and freeze-dried. The weight average MW of dialyzed Merquat 100 is 2×10^5 by static light scattering (14). While this sample is quite polydisperse, we have found, somewhat surprisingly, virtually no influence of polydispersity *per se* on the turbidimetric curves (11). Monodisperse samples, $C_{12}E_4$, $C_{12}E_6$, $C_{12}E_8$, and $C_{12}E_{12}$, were from Nikkol Chemical Co., Japan. SDS (purity > 99%) was from Fluka, Switzerland. $C_{12}E_n$ and SDS were used without further purification. The ionic strength was adjusted by using NaCl from Fisher. Milli-Q water was used throughout this work.

Turbidimetry. Turbidity measurements, recorded as 100 − *T*%, were obtained at 420 nm using a Brinkman PC800 probe colorimeter equipped with a 1-cm path length fiber optics probe. Turbidimetric ‘‘Type I’’ titrations were performed at 24 ± 1°C by adding 60 m*M* SDS in varying ionic strengths [*I*(*M*)] (NaCl) to a solution of 40 m*M* $C_{12}E_n$ [or the mixture of $C_{12}E_n$(s)], 0.5 g/L PDADMAC, also in same *I* with all solutions filtered through a 0.45 μm Whatman filter before titration. All measured values were corrected by subtracting the turbidity of a polymer-free blank.

Electrophoresis. Capillary electrophoresis measurements were made on a Beckman Instruments P/ACE 2000 with UV detection at 200 nm and a voltage of 15 kV. A 50 μm (i.d.) × 40 cm (effective length) capillary was kept at 25 ± 0.1°C. The mobility can be calculated using the relationship

$$\mu = (\ell L(t_0 - t_s)/t_0 t_s)E^{-1} \quad (\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}) \qquad [2]$$

where ℓ is the effective length and L the total length of the capillary (both in cm), t_s and t_0 are retention times (s) of sample and a nonelectrophoresing reference material (methanol), and E is the electric field (volt). The mobile phase was either 0.05 *M* Na borate (pH 9.14) or 0.01 *M* Na acetate + 0.09 *M* NaCl (pH 6.07). Higher ionic strengths would limit the selection of appropriate voltages. As reference compounds, the mobilities of SDS micelles and BSA were measured in 0.01 *M* (pH 6.94) Na phosphate buffer + 0.03 *M* NaCl, giving values of -3.0×10^{-4} and -1.3×10^{-4} cm²/V s for SDS and BSA, respectively, in good agreement with those reported by Nakagawa (15) and Sasa (16).

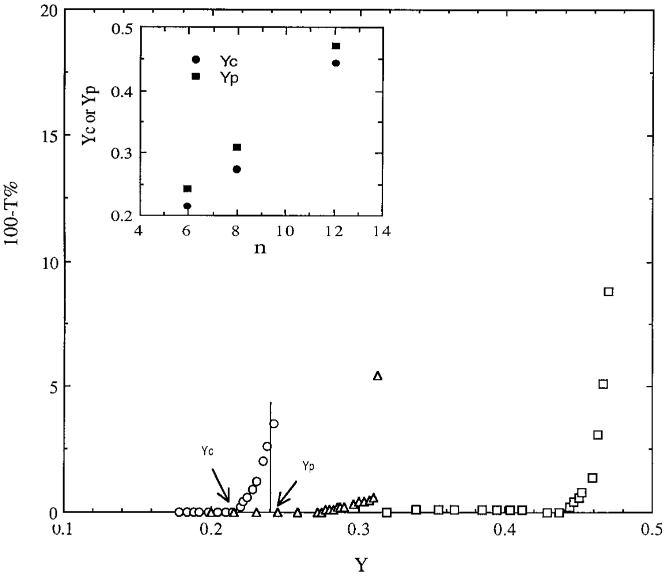

FIG. 1. Type I titrations of $C_{12}E_n$ (40 mM) + PDADMAC (0.5 g/L) with SDS (60 mM) in 0.4 M NaCl, 24°C. $C_{12}E_6$ (○), $C_{12}E_8$ (△), $C_{12}E_{12}$ (□). Inset: dependence of critical Y values on EO chain length.

Quasielastic Light Scattering. Micellar sizes were determined with a DynaPro 801 (Protein solutions Inc.,), which employs a 30-mW solid-state 780-nm laser and an avalanche photodiode detector. Samples prepared in pH 9.1, 0.05 M Na borate buffer were introduced into the 7-μl cell via 0.1-μm Anotec filters. The 90° scattering data were analyzed via the method of cumulants.

RESULTS AND DISCUSSION

1. *Effect of EO Chain Length*

Figure 1 shows the results of type I titrations of $C_{12}E_n$/SDS–PDADMAC systems in 0.4 M NaCl. As noted above, no turbidity is observed until the mole fraction of SDS reaches Y_c, corresponding to some critical micelle surface charge density, σ_c. Just above Y_c, the turbidity increases but the system still remains transparent and stable, indicating that the complexes formed are water-soluble. When Y reaches Y_p, bulk phase separation occurs. One clearly sees effect of EO chain length on Y_c and Y_p: both increase strongly with EO chain length.

In order to substantiate the identification as ‘‘soluble complexes’’ of the species at $Y_c < Y < Y_p$ (as opposed to ‘‘preprecipitates’’), we confirmed the stability of the transmittance measurement (99.2%) over several hours for $C_{12}E_8$/SDS–PDADMAC in 0.4 M NaCl at $Y = 0.30$, i.e., immediately prior to the phase separation point $Y_p = 0.31$. We also found rapid reversibility of the turbidity with respect to Y in the range $0.28 < Y < 0.31$.

We propose that the influence of EO chain length on Y_c has two aspects. The first is to increase the average distance between the bound polycation segments and the SDS sulfate groups by sterically hindering the approach of the former. The second is to increase the distance between micellar SDS head groups though steric repulsion among EO head groups. Both phenomena cause a reduction of the potential ψ at the position of closest approach of bound polycation segments to the micellar sulfate groups. Since the positions of both these groups are best represented by some unknown distribution functions, a rigorous analysis would be difficult. However, we can qualitatively suggest that the position of the sulfate groups is primarily determined by the hydrophobic interaction between the SDS alkyl chains and those of $C_{12}E_n$. Thus, the sulfate groups presumably lie at the edge of the ‘‘hydrophobic core’’. The mean locus of these groups establishes a quasispherical surface with a high negative surface charge density that depends on Y. The segments of the polycation, in its bound state, reside at some average distance from this surface, which we designate as x'_n, and which must increase with the length of EO group, n. The significance of x'_n is shown schematically in Fig. 2.

If x'_n represents the closest position accessible to the bound polycation segments, we may propose that binding occurs when the potential $\psi'_n = \psi_{\text{crit}}$, corresponding to $Y = Y_c$. In the Debye–Hückel approximation

$$\psi(x) = \psi_0 \exp(-x/\kappa^{-1}), \qquad [3]$$

where ψ_0 is the surface potential of the locus of SDS headgroups, and x is the distance from the mean locus of SDS head groups away from the hydrophobic core. Therefore, the potential at the closest accessible position must be higher for shorter EO chain micelles than for longer EO chain-containing micelles at the same Y value. Thus, an increase in n produces a decrease in ψ'_n which must be compensated for by an increase in ψ_0, corresponding to an increase in Y.

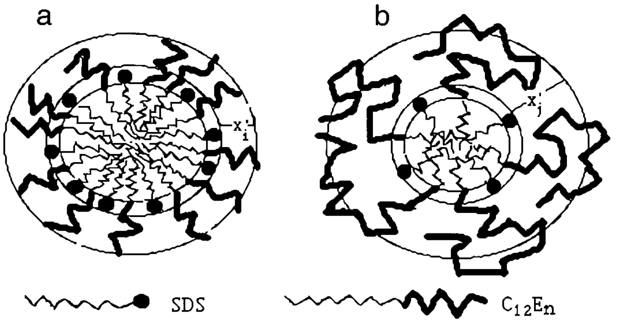

FIG. 2. Schematic presentation of the effect of the EO chain length on the average distance (x'_n) between the SDS head groups and bound polycation segments (polycation not shown). (a) represents shorter EO chain-containing mixed micelle (n = i), and (b) represents longer EO chain-containing mixed micelle ($n = j$, $x'_j > x'_i$).

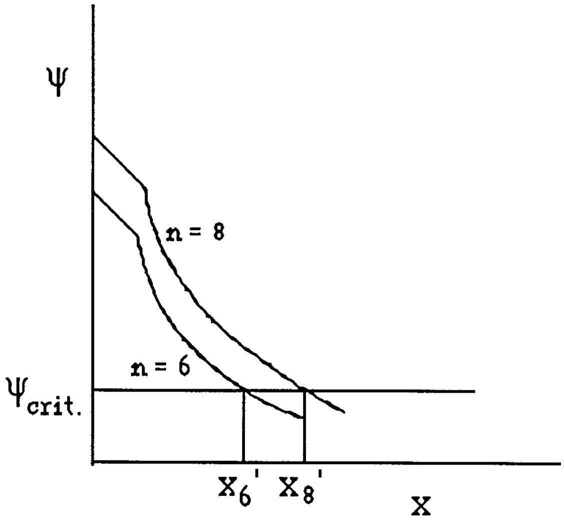

FIG. 3. Schematic view of the effect of EO chain length for mixed micelles containing $C_{12}E_6$ and $C_{12}E_8$, respectively. $\psi_{\text{crit.}}$ corresponds to the value of the potential at $x = x'_n$ (see Fig. 2) at the onset of complexation. x'_6 and x'_8 represent the positions of closest access for the bound polycation segments.

This relationship is schematically presented by Fig. 3. Here, the outer region of the EO layer (region II) contains mobile ions which follow a Boltzmann distribution. The linear part of the curves describes the relationship between $\psi(x)$ and x within the ''Stern layer'' (region I), which may be considered as the domain of ''bound'' counterions, although a dynamic description of these ions is not a concern here.

The second (''lateral'') effect comes from steric repulsion among the headgroups of the EO chains. Results from lamellar phase X-ray diffraction have shown that the mean head group surface area, A, of $C_{12}E_n$ increases with the number of oxyethylene groups (42.6, 45.4, 48.0, and 54.2 Å^2 for $n = 4$, 5, 6, and 7, respectively) (17). This effect leads to an increase in the space between SDS head groups and a decrease in the surface charge density of the micelle.

To prove our hypothesis concerning the effect of EO chain length, we measured electrophoretic mobilities by CE in 0.05 M Na borate. The ionic strength used for the turbidity titrations of Fig. 1 is too high to permit an appropriate voltage for CE. As shown in Table 1, the micelle size (18) at constant I and Y is not affected much by n for $6 \leqslant n \leqslant 12$, so the analysis of the effect of n on the mobility is simplified.

As seen from Table 1, the absolute mobility of the micelle also decreases with increasing EO chain length, indicating that the potential at the shear plane is decreasing with increasing n. The effect might arise from an increase in the average distance between SDS head groups and the shear plane. Alternately, it could be due to an increase in the mean surface area per head group, A, as follows: If the micelles remain spherical with nearly constant R_h (as seen in Table 1 for $n > 4$) an increase in A would correspond to a smaller aggregation number, N. The number of negatively charged head groups per micelle is Ny, where y is the microscopic mole fraction of anionic surfactant. At surfactant concentration well above the cmc, we assume that $y \approx Y$; therefore a decrease in aggregation number at constant Y leads to a decrease in net charge and thus to a decrease in mobility.

It is interesting to note that the sizes of the mixed micelles for $6 \leqslant n \leqslant 12$ are nearly independent of n (Table 1), especially since it has been shown that the size of $C_{12}E_n$ in the absence of ionic surfactant decreases with increasing n (20). In the spherical state, micelles containing longer EO chain would be expected to be larger. However, if the EO chain is sufficiently disordered, like polymer chains, then polyoxyethylene chains extending from the micelle core are randomly coiled, with the thickness of the EO layer approaching an approximate square-root dependence on the number of polyoxyethylene units as n becomes large. The necessary increase of the steric repulsion between the head groups with EO number simultaneously causes an increase of hydrocarbon chain disorder and consequently a reduction of the thickness of the hydrophobic core d_{hc}. Thus, Klose (17) showed that d_{hc} decreases with increasing n ($d_{\text{hc}} = 15.4$, 14.5, 13.7, and 12.1 Å for $n = 4$, 5, 6, and 7, respectively). Therefore, the increase of micelle size arising from an increase in the thickness of the EO layer with n could be compensated by a decrease in d_{hc}, as shown schematically in Fig. 2. Implicit in this analysis is that the change in aggregation number for SDS/$C_{12}E_n$ with n is small for $6 < n < 12$. Indeed, aggregation numbers of 90 (21) and 123 (21) have been reported for $C_{12}E_8$, which bracket the value of 110 reported for $C_{12}E_6$ (23). It is unlikely that the dependence of aggregation number on n would be stronger for SDS/$C_{12}E_n$ than for the pure nonionic micelles.

In order to test the hypothesis implicit in Fig. 3, it was necessary to measure the mobilities at Y_c for different n. A solvent with ionic strength 0.1 M and pH 6.07 was chosen to be compatible with both CE and turbidimetric titration. Table 2 shows results for different n at $Y = Y_c$, where Y_c was obtained from type I titrations, also at $I = 0.1$ M. (Data are not shown for $C_{12}E_4$/SDS because this mixture is not soluble at the low Y value corresponding to Y_c at this ionic strength.) It may be seen that the mobility is essentially constant despite a change in Y of as much as 200%. This

TABLE 1
The Sizes and Mobilities (μ) of Mixed Micelles of $C_{12}E_n$ and SDS at $Y = 0.50$, pH 9.14, and $I = 0.05$ M

Compound	$C_{12}E_4$	$C_{12}E_6$	$C_{12}E_8$	$C_{12}E_{12}$
R_h (nm)	4.5	2.0	2.0	2.1
μ (10^{-4} cm^2 V^{-1} s^{-1})	−3.2	−3.1	−2.9	−2.3

TABLE 2
Mobilities of Mixed Micelles in Different Combinations at their Y_c in pH 6.07, $I = 0.1$ M

SDS + $C_{12}E_n$	$C_{12}E_6$	$C_{12}E_8$	$C_{12}E_{12}$
Y_c	0.06	0.08	0.12
μ (10^{-4} cm^2 V^{-1} s^{-1})	−0.31	−0.32	−0.32

result can be explained by hypothesizing that a decrease in $\psi(x')$ (the potential at the distance of closest approach of polyion segments) due to EO chain length effects is exactly compensated for by an increase in ψ_0 accomplished by raising Y (see Fig. 3).

2. Effect of EO Chain Length Distribution

Shown in Fig. 4 are ''type I'' titrations with SDS for systems with different combinations of $C_{12}E_n$ but at constant total concentration of nonionic surfactant. Also, for comparison, the plot for pure $C_{12}E_8$ is included. The effect of the mole fraction of the higher MW nonionic surfactant [$R = [C_{12}E_{12}]/\{[C_{12}E_{12}] + [C_{12}E_4]\}$] is easily seen by comparison of the curves for $R = 0.20$, 0.25, and 0.33, for which $Y_c = 0.17$, 0.18, and 0.23, respectively. This effect is as expected from the previous discussion, i.e., due to the increase in the distance of closest approach of polyion segments. However, the effect of R on Y_p is much more dramatic (e.g., from 0.21 to 0.35, as R increases from 0.20 to 0.33) with the result that $\Delta Y = Y_p - Y_c$ increases strongly with R. For the case of $R \geqslant 0.20$, a maximum even appears, as is observed for the system TX-100/SDS–PDADMAC (5). Similar results (not shown) are obtained for mixtures of $C_{12}E_{12}$ and $C_{12}E_6$.

In an earlier study of PDADMAC–TX-100/SDS complex formation (5) the region of soluble complex formation, $Y_c < Y < Y_p$, was explained on the basis of micelle compositional polydispersity, in which it was recognized that the bulk mole fraction Y is an average from which the compositions of individual micelles will deviate. One could then visualize a microscopic composition y_c such that micelles with $y > y_c$ bind to polymer. Such ''active micelles'' first appear at $Y = Y_c$ and then increase in number, with a corresponding increase in turbidity, until the available chains are saturated. Little subsequent change in turbidity with Y occurs until micelles have sufficient charge density to intimately ion pair with the polycation, leading to phase separation at Y_p. In support of this description, we recently reported on the compositional heterogeneity of such mixed micelles by capillary electrophoresis (24). However, such arguments do not account for the striking difference between Triton X-100 and $C_{12}E_n$.

We propose that the polydispersity of EO chain length plays an important role. At fixed y, some micelles have a larger relative concentration of short EO chains, with a higher ''surface'' potential $\psi(x')$. Polycation will preferentially bind to such micelles. Unbound micelles will be rich in longer-EO chains, which now absorb further increments of SDS. Such effects delay the formation of micelles with surface charge densities large enough to lead to phase separation. An additional effect is the larger hydration for longer EO chains [the number of water molecules per EO group is 4.2 for $C_{17}E_{16.4}$, and 12.4 for $C_{16}E_{63}$ (25)]. Complexes formed with micelles rich in longer EO chains are more strongly hydrated with less tendency to phase separate.

Further comparisons are possible between systems that have similar ''average'' EO chain length, namely, $C_{12}E_8$/SDS and $C_{12}E_4/C_{12}E_6/C_{12}E_8/C_{12}E_{12}$ (1:1:1:1)/SDS. The difference between these two plots in Fig. 4 clearly shows that mixing different nonionic surfactants produces an effect related to surfactant heterogeneity. These two systems also show a more pronounced difference in Y_p vs Y_c, which might suggest that Y_c is mainly determined by the average EO chain length, while Y_p is more strongly influenced by the presence of longer chains.

The maximum value of $Y_p - Y_c$, corresponding to the broadest range of soluble complex formation, was observed at 3:1 $C_{12}E_4$:$C_{12}E_{12}$. When the fraction of the longer EO chains is high, the dependence of $\psi(x')$ on Y will be close to that of micelles composed of $C_{12}E_{12}$ alone since the surface of the micelle is essentially covered by longer EO chains.

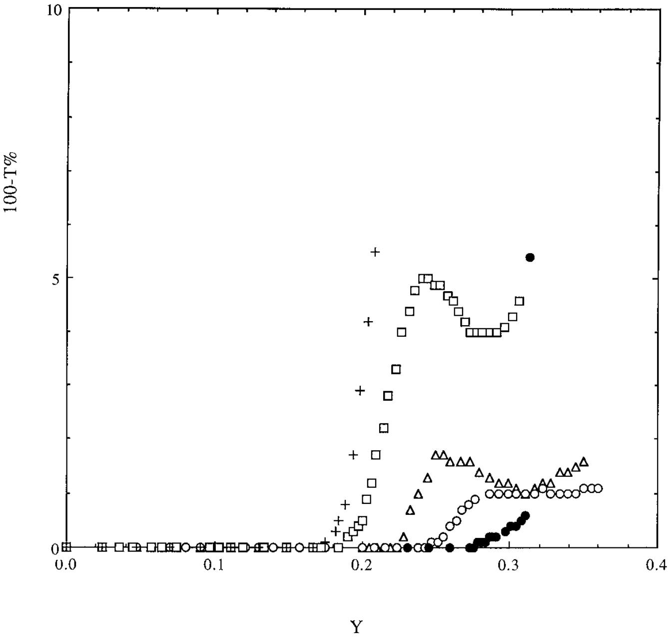

FIG. 4. Type I titrations of mixed $C_{12}E_n$ (40 mM) + PDADMAC (0.5 g/L) using SDS (60 mM) in 0.4 M NaCl. $C_{12}E_4/C_{12}E_{12}$, mole fractions of $C_{12}E_{12}$: 0.20 (+), 0.25 (□), 0.33 (△). $C_{12}E_8$ alone (●). $C_{12}E_4/C_{12}E_6/C_{12}E_8/C_{12}E_{12}$ = 1:1:1:1 (○).

As a result, Y_c increases. On the other hand, if the fraction of longer EO chains is small, the majority of micelles are rich in shorter EO chains, and the surface charge density increases rapidly with Y, resulting in early phase separation. Both effects lead to a narrow range of soluble complex formation. Thus, the maximum in $Y_p - Y_c$ is observed at an intermediate ratio of $C_{12}E_4$:$C_{12}E_{12}$. We can also envision that polycations initially bind to $C_{12}E_{12}$-poor micelles (which have higher surface potentials), but that additional SDS goes preferentially into $C_{12}E_{12}$-rich micelles, delaying the formation of micelles with large enough ψ_0 to cause phase separation.

CONCLUSION

Turbidimetry, capillary electrophoresis, and dynamic light scattering were used to study the complexation of polydiallyldimethylammonium chloride (PDADMAC) with mixed micelles of sodium dodecyl sulfate (SDS) and dodecanol ethoxylates ($C_{12}E_n$). The results show that the onset of the binding of PDADMAC to mixed micelles and bulk phase separation are both affected by the EO chain length and distribution of $C_{12}E_n$. The mole fraction (Y) of SDS in the mixed micelle required to form the complex (Y_c) and bulk phase separation (Y_p) both increase with n. The electrostatic nature of the onset of binding was demonstrated by electrophoretic mobility measurements: although Y_c varies with n, the electrophoretic mobility of mixed micelles with composition corresponding to Y_c is independent of n. Broader distributions of EO chain length cause broader regions of formation of soluble complex, which may be attributed to the polydispersity of EO chain length in the micelles. The presence of longer EO chains hinders the increase of the potential at the locus of polymer binding as Y increases, resulting in an expansion of the region of soluble complex formation.

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