

Critical Conditions for the Binding of Polyelectrolytes to Small Oppositely Charged Micelles

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Mixed micelles associate with polyelectrolytes of opposite charge to form soluble or insoluble complexes. The interaction takes place abruptly—signaled by a sudden enhancement in scattering—upon an increase of micelle surface charge density, an increase in polymer linear charge density, or a decrease in ionic strength, and involves a microscopic or macroscopic phase change. Because the surface charge state and the dimensions of the mixed micelles may be varied over a wide range, the polyion-micelle system provides a useful model for polyelectrolyte-colloid interactions. Turbidimetric titrations have been carried out over a range of ionic strengths for two systems. One is composed of cationic/nonionic micelles of dimethyldodecylamine oxide (DMDAO) in the presence of the strong polyanion poly(2-acrylamido-2-methylpropanesulfonic acid, sodium salt) (PAMPS) or its lower charge density copolymer with *N*-vinylpyrrolidone (P(AMPS-NVP)). The other consists of mixed anionic/nonionic micelles of sodium dodecyl sulfate (SDS) and dodecylhexa(oxyethylene) glycol (C₁₂E₆) in the presence of the polycation poly(dimethyldiallylammonium chloride) (PDMDAAC). The results provide the ionic strength dependence of the critical micelle composition for polyion-micelle association. From these experimental phase boundaries, along with appropriate potentiometric or fluorescence probe measurements, we obtain the critical micelle surface potential. For both systems, the critical surface charge density (σ_c) is observed to depend on the square root of the ionic strength (I). This result is particularly meaningful in the DMDAO systems, in which the absence of bulky surfactant headgroups means that σ_c can be clearly defined. Furthermore, in this work we focus exclusively on the pH and I region in which the micelle maintains constant spherical shape. The observations for the DMDAO system may then be compared to relevant theories for the interaction of polyelectrolytes with oppositely charged surfaces. In addition, we suggest a simplified treatment for a spherical charged surface which yields the observed $\sigma_c \sim I^{1/2}$ relationship. Analyses of the electrostatic potential decay curves for the systems DMDAO-PAMPS and DMDAO-P(AMPS-NVP) at critical conditions suggest that the mean position of polyion segments binding to the micelle is about 6 Å from the micelle surface and that a potential of +5 mV at this location is required for binding to take place. For mixed micelles of SDS/C₁₂E₆ with PDMDAAC, it appears that the oxyethylene head groups obstruct the approach of the polycation, so that the distance between polyion segments and the sulfonate head groups is more difficult to define.

Introduction

The interaction of polyelectrolytes with oppositely charged particles is an important phenomenon in commercial processes and in biological systems. Some examples of the former are as follows: water treatment by colloidal flocculation with polyelectrolytes,¹ flocculation of cellulosic fibers in paper making,² recovery of mineral suspensions,³ precipitation of bacterial cells with polycations,⁴ and the stabilization of concentrated preceramic suspensions.⁵ Examples involving biopolymers include the immobilization of enzymes in polyelectrolyte complexes,⁶ purification of proteins by selective precipitation and coacervation,⁷ and the nonspecific association of DNA with basic proteins.⁸

The binding of polyelectrolytes to oppositely charged particles and surfaces has been the subject of extensive theoretical investigation. The adsorption of polyions on planar charged surfaces was treated for example by Wiegelt,⁹ by Scheutjens, Fleer, and co-workers,¹⁰ and by Muthukumar.¹¹ Odijk considered the binding of a flexible polycation to a rigid charged cylinder.¹² Without a detailed comparison of these treatments, one may point out that all of them lead to prediction of a phase transition; binding of the polyion is predicted to occur abruptly upon sufficient change of any of the four important variables: ionic strength (I), the charge per polymer repeat unit (q), particle surface charge density (σ), or temperature. The interpretation of the role of the last parameter in these theories is unlikely to survive experimental test, since such important effects as the entropy of released microions, alterations in water structure, and changes in the hydration of ions are not adequately considered. With regard to the other variables, however, it is intuitively obvious that the magnitude of the electrostatic interaction between polyelectrolyte and particle should increase with σ and q and diminish with I , and all treat-

ments agree in this regard. Disagreement appears in the scaling of these variables at critical conditions, but few experimental tests of these relationships have appeared.

Aqueous systems containing polyelectrolytes and oppositely charged micelles provide a model for the coulombic interaction of polyelectrolytes and charged colloids,¹³⁻¹⁹ and the phenome-

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nology of such systems may guide the development of theory.²⁰ The micelle "surface" charge density (σ) may be varied either by controlling the composition of mixed ionic/nonionic micelles¹³⁻¹⁶ or by adjusting the pH when the micellar surfactant carries a titratable head group.¹⁷ σ may be quantitatively determined by calculations involving the micelle aggregation number and effective head group area contributions, via measurements of the surface potential ψ_0 and application of the Gouy-Chapman equation, or by some similar relationship between σ and ψ_0 . This last parameter in turn can be obtained using fluorescent or titratable probes of the micelle surface¹⁵ or—in certain cases—by potentiometric titration of the surfactant head group itself. In addition to varying σ , it is possible to control the micelle dimensions (and therefore its mean curvature) by controlling the geometry of the surfactant molecules and the micelle composition.²¹ Of particular interest are changes observed in the aggregation order of the polymer-micelle complex when the relative size of two macroionic species changes.¹⁸

In this study we report on the critical association of a cationic polyelectrolyte with mixed anionic/nonionic micelles of sodium dodecyl sulfate and $C_{12}E_6$ and particularly on the association of anionic polyelectrolytes with micelles of dimethyldodecylamine oxide (DMDAO). The latter system is especially attractive for such studies for several reasons. (1) Most nonionic surfactants have very large headgroups, which confounds the conception of the micelle "surface"; owing to an intense amine oxide dipole, DMDAO on the other hand can form a soluble uncharged micelle even though the headgroup is small. (2) The amine oxide groups may be protonated over the pH range $3 < \text{pH} < 9$, and from the measurable apparent $\text{p}K_{\text{a}}$, one may determine the surface potential.²³ (3) DMDAO micelles are compact spheres over a reasonable range of pH and ionic strength;²⁴ this simplifies electrostatic considerations. The association of DMDAO with polyanions is found to exhibit a phase transition, which occurs abruptly upon increase in the mean degree of protonation (β) or decrease in ionic strength (I). The phase formed at large β or low I is a liquid coacervate; studies with related systems suggest that it arises from the aggregation of polyelectrolyte-micelle complexes whose net charge is close to neutrality.¹⁸ The dependence of β on I at critical conditions may be viewed as a phase boundary and yields the relationship between σ_c and I . In ref 17, we noted that this dependence changed abruptly in the range of β and I where the micelle exhibits a transition from spherical to rodlike dimensions. In that work, we reported approximate values for σ_c (based solely on applications of the Gouy-Chapman equation) and provided only a phenomenological account of the interdependence of σ_c and I . We carried out those studies with commercially available samples of sodium poly(styrenesulfonate) (NaPSS), which subsequent characterization data showed to be of uncertain homogeneity.²² In the present study, we deal only with the spherical regime of DMAO micelles ($0 < I < 0.25$; $6.5 < \text{pH} < 8$) and determine σ_c by use of several procedures. We employ two well-characterized polyanions synthesized specifically for this study. We now place the phase boundary results in the context of available relevant theories and also provide a simple model for binding to a spherically charged colloid, which shows agreement with the phenomenological results. Previously obtained

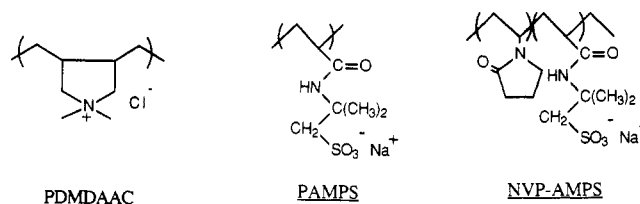


Figure 1. Structure of polyelectrolytes used in this study.

results for the system $C_{12}E_6$ -SDS/PDMDAAC are used to calculate σ_c for that system in order to demonstrate the general nature of the dependence of σ_c on I .

Experimental Section

DMDAO, "purum" grade from Fluka (Happague, NY), was found to contain 1.3% H_2O by Karl Fisher titration. pH titration in acetic acid with $HClO_4$ to the acid end point only consumed 97.2% of the theoretical amount of acid, from which it was concluded that the surfactant was partially in the salt form, perhaps because of adsorption of CO_2 . Therefore, solutions of DMDAO were adjusted by addition of NaOH to pH ca. 11 prior to titration with HCl. $C_{12}E_6$ was purchased from Nikko Chemical Co. (Tokyo). SDS was puriss grade from Fluka (Happague, NY). Poly(dimethyldiallylammonium chloride) (PDMDAAC), a strong polycation, was a commercial sample ("Merquat 100") from Calgon (Pittsburgh, PA). After dialysis and freeze-drying, the weight-average molecular weight was determined by light scattering as 2.5×10^5 .²⁵ A homopolymer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) (Lubrizol Corp., Wickliffe, OH) was prepared by free radical polymerization of a 10 wt % solution of the neutralized monomer in deionized water at 65–70 °C, under N_2 , with $Na_2S_2O_5$ and $(NH_4)_2S_2O_8$ (both from Aldrich) as initiator. The molecular weight (MW), estimated from the measured intrinsic viscosity of 1.21 dL/g in 0.50 M NaCl, was 6×10^5 (using the relationship²⁶ $[\eta] = 1.95 \times 10^{-5} (M_w)^{0.83}$). A copolymer of AMPS with *N*-vinylpyrrolidone (NVP) (Aldrich) was prepared by a similar procedure. The intrinsic viscosity in 0.50 M NaCl was 3.30 dL/g, indicating a MW of ca. 2×10^6 . Elemental analysis showed a ratio of AMPS:NVP of 64:36 (mole basis). Structures of these three polymers are in Figure 1.

The relationship between pH and the degree of protonation of DMDAO micelles (β) was obtained by pH titrations of 50 mM DMDAO using an Orion Model EA 920 meter equipped with an Orion glass/combination Ross electrode. The pH was first adjusted to 10.9 with 1.0 M NaOH, then titrated under N_2 atmosphere with 0.500 M HCl. After correction by subtraction of the titration curve of a surfactant-free blank,²⁷ the $\beta = 1$ equivalence point was determined by fitting the titration data at low pH to a cubic equation, differentiating it manually, and setting the second derivative to zero. The $\beta = 0$ end point was obtained from a plot of the first derivative of the raw titration data. All other measurements involving DMDAO were carried out in the regime of low ionic strength, $I < 0.3$, to ensure spherical micelle dimensions.^{24,27}

The dimensions of the DMDAO micelles were measured by dynamic light scattering with 90° detection, using one of two systems. The first was composed of a Jodon 20-mW He:Ne laser, a Malvern RR102 spectrometer, and a Nicomp T1000D 64 channel autocorrelator interfaced with a Epson Equity II computer (this system and experimental procedures have been previously described¹⁵). The second was an Oros Model dp-801 QELS instrument (Biotage, Charlottesville, VA) equipped with a 7- μ L sample cell maintained at 26.5 ± 0.4 °C, a 30-mW solid-state laser (780 nm), and an actively quenched avalanche photodiode. For either instrument, samples of DMDAO, 30–100 mM, adjusted to the desired pH and ionic strength, were filtered through 0.2- μ m Anotec filters prior to data collection. There were no significant

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(22) Elemental analysis of dialyzed and freeze-dried samples of the NaPSS polymers used in ref 17 yield degrees of sulfonation ranging from 82 to 86%. This result, along with the occasional turbidity and filtration behavior of some of these materials, suggests the possibility of considerable compositional heterogeneity and concomitant uncertainty about the charge density.

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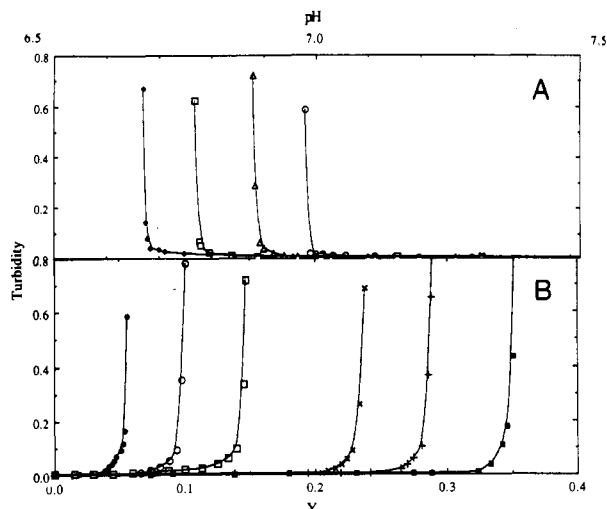


Figure 2. "Type 1" turbidimetric titrations: (A) PAMPS-DMDAO (axis above); ionic strengths (from left to right) 0.25, 0.20, 0.15, and 0.10 M. (B) PDMDAAC- $C_{12}E_6$ /SDS (axis below). Ionic strengths (from left to right) 0.05, 0.10, 0.20, 0.40, 0.60, and 0.80 M. Polymer concentration 0.50 g/L, $C_{12}E_6$ concentration 20 mM.

differences between the mean apparent diffusivities obtained using the two different instruments.

"Type 1" turbidimetric titrations¹⁷ for DMDAO in the presence of polyanions were carried out as follows. DMDAO (50 mM) and 0.50 g/L polymer were combined at the desired ionic strength (adjusted with NaCl) and at pH ca. 9. HCl (0.499 M) was added with a Gilmont 0.200-mL microburet, and the pH and transmittance were simultaneously monitored, the latter at 420 nm using a Brinkmann colorimeter, equipped with a 2 cm path length fiber optics probe. Distilled water was used to set the colorimeter to 100%T prior to each titration. Measured values of 100 - %T (linearly proportional to the turbidity for %T > 90) were corrected by subtraction of a blank, consisting of a polymer-free solution. The pH at which an abrupt increase is observed (see Figure 2A) is defined as pH_c and corresponds to the onset of complex formation. From pH titration curves obtained as mentioned above, pH_c was converted to β_c . In the case of the SDS/ $C_{12}E_6$ -PDMDAAC system, the micelle surface charge density is controlled by Y , the mole fraction of SDS in the mixed micelle. Therefore, type 1 titrations were carried out by adding 40 mM SDS to a solution of 0.50 g/L PDMDAAC and 20 mM $C_{12}E_6$, with both titrant and solution adjusted to the appropriate ionic strength by addition of NaCl. 100 - %T readings were corrected by subtraction of turbidity values for a polymer-free blank. Y_c was determined as the surfactant composition at which an abrupt turbidity is initiated (see Figure 2B). Surface potentials of $C_{12}E_6$ /SDS micelles at I and Y corresponding to the critical conditions defined as in Figure 2B were determined by means of fluorescent or potentiometric probes, as previously reported.¹⁵

Results and Discussion

Phase Boundaries. Critical conditions for complexation may be described by a phase boundary, as shown in Figure 3, in which we plot the dependence of Y_c on ionic strength for the system PDMDAAC-SDS/ $C_{12}E_6$. As noted previously,¹³ such phase boundaries are independent of the concentration of polymer or micelle. This is because they reflect only the local interaction of a sequence of polymer segments with the micelle surface, which has a surface charge density σ . The dependence of σ on Y is given by

$$\sigma \sim \frac{Y}{A_N + (A_A - A_N)Y} \quad (1)$$

where A_N and A_A are the effective molecular head group areas of nonionic and anionic surfactants, respectively. (With units of esu/cm^2 for σ and $\text{cm}^2/\text{molecule}$ for A , the proportionality constant is the charge per ionic headgroup.) Since A_N and, especially,

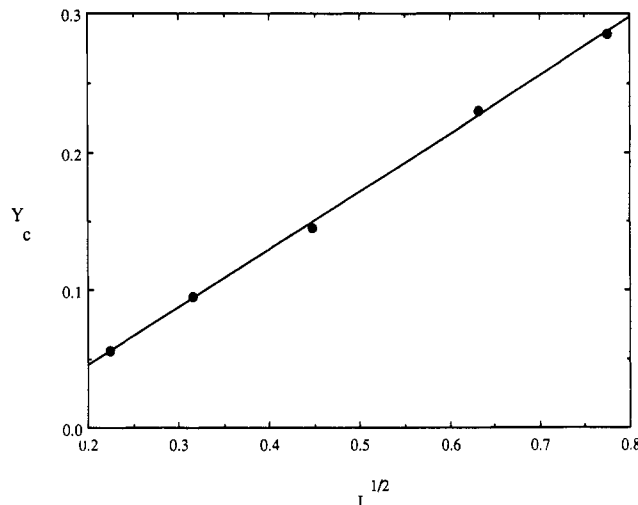


Figure 3. Dependence of critical micelle composition on ionic strength for PDMDAAC- $C_{12}E_6$ /SDS (from data of Figure 2B). The homogeneous solution phase exists to the right and below the line.

TABLE I: Measured and Calculated Quantities for SDS/ $C_{12}E_6$ Mixed Micelles at Conditions Corresponding to Critical Binding with PDMDAAC

I, M	Y_c	$R_h, \text{\AA}$	$\Psi_o^{\text{HHC}},^b$ mV	$\Psi_o^{\text{DA}},^c$ mV	$10^9 \sigma^{\text{HHC}},^d$ esu cm^{-2}	$10^3 \sigma^{\text{DA}},^e$ esu cm^{-2}
0.05	0.056	72	-12	-11	-2.1	-2.0
0.10	0.095	75	-18	-8.8	-4.5	-2.2
0.20	0.145	91	-20	-13	-6.6	-4.2
0.40	0.230	137	-21	-10.6	-9.4	-4.7
0.60	0.285	194	-22	-11	-11.7	-5.8

^a By QELS. ^b From pK of HHC probe solubilized in micelle.¹⁵

^c From pK of dodecanoic acid probe solubilized in micelle.¹⁵ ^d From columns 3 and 4, via eq 2. ^e From columns 3 and 5, via eq 2.

A_A are complex functions of Y and I ,^{20b} we measure the surface potential ψ_o and then deduce σ via the linearized Gouy-Chapman (G-C) equation for a sphere of radius a

$$\sigma = (\epsilon \psi_o / 4\pi) (\kappa + 1/a) \quad (2)$$

where ϵ is the solvent dielectric constant. In the case of SDS/ $C_{12}E_6$ micelles, ψ_o may be measured using amphiphilic probe molecules, namely dodecanoic acid (DA) and heptadecylhydroxycoumarin (HHC), by a procedure described elsewhere.¹⁸ Under conditions of I and Y corresponding to the phase boundary of Figure 3, the HHC probe yields potentials ranging from -12 to -22 mV as one progresses along the phase boundary in the direction of increasing Y , while ψ_o for the DA probe under the same set of conditions is virtually constant at -11 ± 1 mV.¹⁸ This difference is probably a result of the greater hydrophobicity of HHC which allows the probe to reside in the more interior region of the micelle, closer to the mean locus of the sulfonate groups; the DA head group, on the other hand, may hydrogen-bond to the polyether head groups and is likely to be more distal with respect to the micelle core. We proceed to evaluate σ_c with both sets of data, using values for the radii of the mixed micelles obtained by QELS. Application of the linearized G-C equation for spherical particles then yields the surface charge densities shown in Table I.²⁸

In Figure 4, we plot the ionic strength dependence of σ_c obtained with the two probes. It can be seen that both sets of data reveal, within experimental error, a linear dependence of σ_{crit} on $I^{1/2}$ (the regression coefficient for the data obtained with DA probe is better

(28) The dimensions of the $C_{12}E_6$ /SDS mixed micelles suggest that a cylindrical model could be more realistic. Numerical solutions of the expression analogous to eq 2 for cylindrical colloid²⁹ were carried out. For $I < 0.4$, the results were identical, but at the largest ionic strength, the approximation of spherical geometry introduces ca. a 10-15% negative error in calculated values of σ . Corrections for this would slightly improve the linearity of the plots in Figure 3.

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TABLE II: Dimensional and Electrostatic Properties of DMDAO Micelles at pH and Ionic Strengths Corresponding to Critical Conditions for Binding of PAMPS

<i>I</i> , M	pH _c ^a	β ^b	Ψ ₀ mV ^c	R _n ^d Å	R' ^e Å	<i>n</i> '	10 ³ σ _g ^f esu cm ²	10 ³ σ _{GC} ^h esu cm ²
0.10	6.98	0.08	10.7	26	28	95	3.3	3.1
0.15	6.88	0.10	11.8	31	31	110	5.0	3.9
0.20	6.77	0.12	13.0	31	35	135	6.5	4.8
0.25	6.68	0.15	14.6	39	38	170	8.0	5.8

^a At critical conditions (determined from "type 1" turbidimetric titration of polyanion-micelle solution. ^b From pH_{crit}, in conjunction with titration curve. ^c From $-2.303(k_B T/e)(pK_\beta - pK_0)$ (see ref 21). ^d By QELS. ^e From analysis of titration data (see ref 21). ^f By interpolation of static light scattering data from ref 22. ^g From $ne\beta/4\pi a^2$. ^h From eq 2.

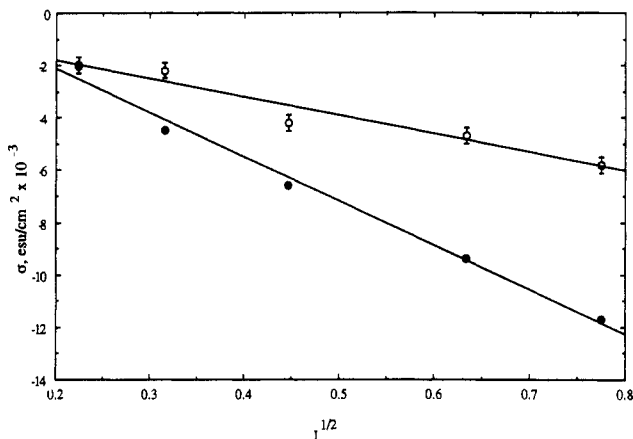


Figure 4. Dependence of critical micelle surface charge density on the square root of ionic strength for the system PDMDDAC-SDS/C₁₂E₆. From data of Figure 3, heptadecylhydroxycoumarin is used as a probe for the micelle surface potential (lower curve) or dodecanoic acid (upper curve).

than 0.999). However, uncertainty about the probe location, which is a manifestation of the ambiguous nature of the "surface" of this micelle, prompts us to turn to results for the DMDAO-polyanion system for confirmation of this behavior.

In the case of DMDAO, the micelle surface charge density is controlled by the pH via the degree of protonation, β. As seen in Figure 5, β_{crit} is linearly proportional to *I*^{1/2}, for both PAMPS and NVP-AMPS, in the range of ionic strengths examined. Conversion of β_c to σ_c was accomplished in one of two ways. In one procedure, the "geometric" approach, the micelle radius (*a*) was first ascertained either from an analysis of the pH titration data according to the method of Tokiwa²³ or more directly by QELS. σ was then obtained by dividing the total number of charged head groups β*n*—where *n* is the micelle aggregation number—by 4π*a*². In the second procedure, the pH titration curve was used to calculate the electrostatic surface potential ψ₀ at any β and *I*, from the difference between the effective p*K*_β and the intrinsic value (p*K*_β at β → 0).²³ (Here p*K*_β is the apparent logarithmic acid dissociation constant of the protonated amine, given by log [β/(1 - β)]). Since the DMDAO micelle is spherical throughout the ionic strength and pH range involved, we can confidently use eq 2 to calculate σ.

The results of these two calculations are summarized in Table II for the system DMDAO-PAMPS. We note that the radius determined by the analysis of titration data using the method of Tokiwa²³ of 30 ± 5 Å is intermediate between our QELS results of 33 ± 7 Å and the value of 26 ± 1 Å reported by X-ray scattering at pH 4.5 and *I* = 0.10 M.³⁰ However, the "geometric" procedure consistently gave higher values of σ than the latter; we attribute this to the fact that the former method assumes no binding of counterions (i.e. Cl⁻) to the micelle. Therefore, σ from the second method (σ_{GC}) was considered to be more reliable and was subsequently considered alone. Critical β values for P(AMPS-NVP) were analyzed by a similar procedure to yield corresponding micelle surface charge densities at critical conditions for binding of the copolymer. The phase boundaries in Figure

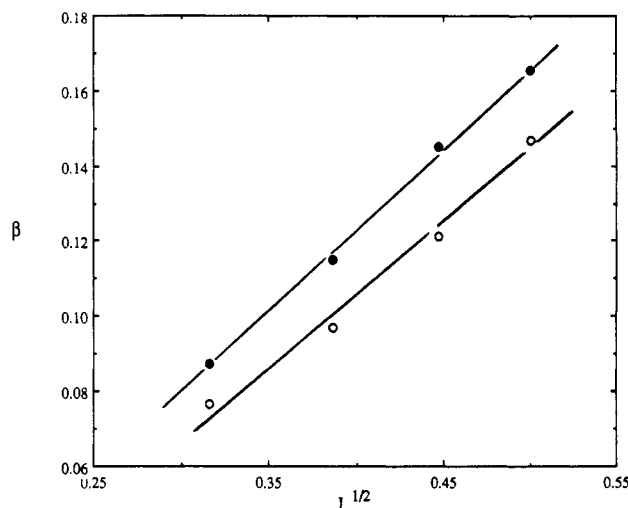


Figure 5. "Phase boundary" for DMDAO-PAMPS (open symbols) and DMDAO-NVP-AMPS (filled symbols) expressed as the ionic strength dependence of the critical degree of protonation of the micellar surfactant.

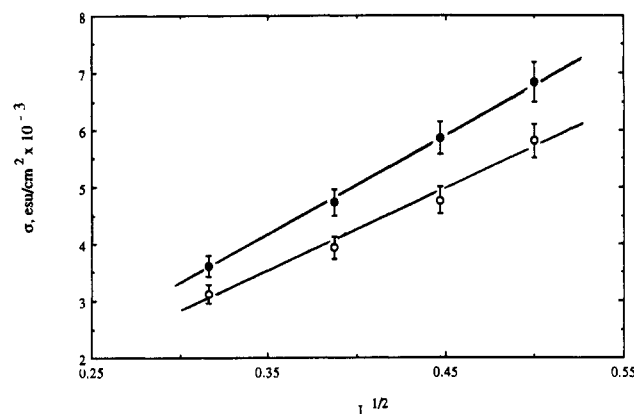


Figure 6. Dependence of micelle surface charge density on ionic strength for DMDAO with PAMPS (lower curve) and PAMPS-NVP (upper curve), from data of Figure 5. Regression coefficients of fitted lines: 0.992 (lower curve) and 0.999 (upper curve).

6 show the dependences of σ_{crit} on *I* for both PAMPS and P(AMPS-NVP).

The linear dependence of σ_{crit} on *I*^{1/2} in Figure 6 confirms the result reported above for the PDMDAAC-SDS/C₁₂E₆ system of reversed charge. We will first discuss this functional relationship, namely that σ_{crit} varies linearly with κ, the Debye-Hückel parameter. We may compare this phenomenological result with several theoretical treatments for the binding of polyelectrolytes to oppositely charged colloids whose surfaces may be treated as charged planes, namely those of Wiegand,⁹ Evers et al.,¹⁰ and a modification of Wiegand's treatment by Muthukumar.^{11a} Considering the adsorption of a charged macromolecule on a surface with a weak opposite charge, Wiegand found a phase transition characterized by the expression

$$|σq| = k_B T (5.7985) κ^3 ε l^2 / 48 π \quad (3)$$

where *q* is the charge on a polymer repeat unit, *k_B* the Boltzmann constant, ε the dielectric constant of the medium, and *l* the length

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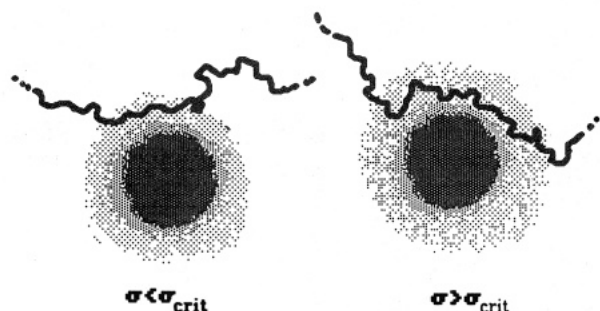


Figure 7. Schematic depiction of the localized binding of polyion to micelle (from ref 15). The stippled area represents the region in which the potential due to the micelle surface is greater than $k_B T/e$.

of a repeat unit. For a given polymer at constant temperature, eq 3 then gives (since ϵ is only weakly dependent on κ) $\sigma_c \sim \kappa^3$, a distinctly different result from what we observe in Figures 4 and 6. More recently, Muthukumar modified the Wiegand treatment by considering the effect of the ionic-strength dependence on the polyion configuration. This leads to a result identical to eq 3, except that l^2 is replaced with l_1^2 , where l_1 is the q -dependent step length, also given by $l\alpha^2$, with α being the Flory expansion factor. Since α varies inversely with ionic strength, hence inversely with κ , the κ dependence on σ_c is substantially diminished but not necessarily to the first power in κ . The presence of a polymer expansion term also leads to a molecular weight effect: since l_1 increases with MW, so does σ_c , yielding the result that lower MW polymers (with smaller l_1) bind more strongly.¹¹ This result is contrary to experimental findings we have reported elsewhere, namely that β_c varies inversely with MW, at least in the regime of I in which DMDAO micelles are rodlike.³¹

A Simple Model. The situation under consideration here is represented schematically in Figure 7. The stippled area represents the region in which the potential due to the colloid surface exceeds $k_B T/e$. Its dimensions depend on the colloid surface charge, curvature, and κ . (Note that this is not the Debye-Hückel ion atmosphere, whose thickness does not depend on σ .) A sequence of polyion segments occupies a position alongside a colloid surface, in a configuration which does not substantially reduce its entropy. One of these sequences with a net charge (Z_T) becomes attached to the colloid surface with a change in electrostatic interaction energy (W_{el}). If this energy is such that $W_{el} > k_B T$, we propose that there will be binding accompanied by the measurable phase transition. It is clear that W_{el} should depend on Z_T and hence on q . The magnitude of Z_T depends also on polyion chain flexibility and on the thickness of the region of high potential surrounding the particle, which in turn increases with the colloid surface charge density and decreases with the ionic strength. Thus, W_{el} should increase with σ and decrease with κ , consistent with our finding that $\sigma_c \sim I^{1/2}$.

To treat the model more quantitatively, while avoiding complicated mathematical formulations, we begin with the rather severe ansatz that the energetics of the cooperative binding of the segment sequence with net charge (Z_T) to an oppositely charged sphere can be approximated by the binding of an equivalent point charge (Z_{eff}). This assumption will be most valid when the distance between the bound polyion segments and the micelle surface is at least a few Debye lengths. The binding energy is then

$$W_{el} = Z_{eff} \int_0^\infty E(x) dx = -Z_{eff} \int_a^\infty \left(\frac{d\psi}{dr} \right) dr \quad (4)$$

where E is the electric field at a distance $x = r - a$ from the colloid surface. Solving eq 4 we obtain

$$W_{el} = Z_{eff} \psi_a \quad (5)$$

which from eq 2 may be written as

$$W_{el} = Z_{eff} (4\pi\sigma/\epsilon_0) (\kappa + 1/a)^{-1} \quad (6)$$

(31) Davis, R. M.; Zhang, H.; Dubin, P. L.; McQuigg, D. W. *Polym. Prepr. Am. Chem. Soc., (Div. Polym. Chem.)* 1991, 32 (1), 126.

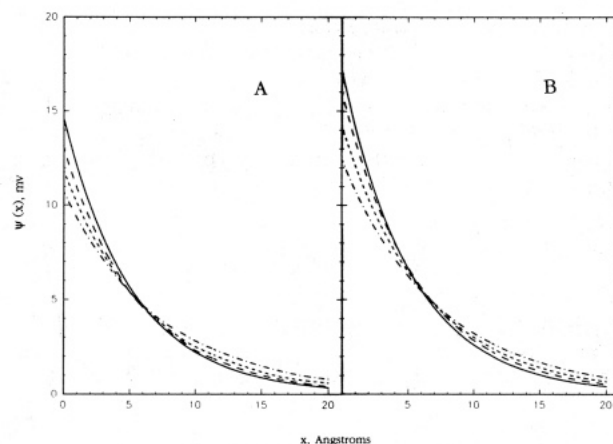


Figure 8. Electrostatic potential in the vicinity of the DMDAO micelle at conditions of ionic strength and pH corresponding to the point of incipient binding of polyion for PAMPS (A) and PAMPS-NVP (B): solid line, ionic strength 0.25 M; broken lines (from top to bottom at $x = 0$), ionic strengths 0.20, 0.15, and 0.10 M.

Note that the measured potentials of 10–15 mV appear to justify the linearization for eq 2 in that we are dealing with $e\psi/k_B T \leq 0.5$. Setting $W_{el} = k_B T$ as the condition for binding gives

$$Z_{eff} \sigma_c = (\epsilon_0 k_B T / 4\pi) (\kappa + 1/a) \quad (7)$$

Note that, in refs 9–11, a is taken as ∞ . In this limit, eq 7 is essentially identical to the result obtained by Evers et al.^{10a} for the adsorption of a weak polyacid onto a positive surface, for the case of complete ionization ($\alpha = 1$) and no non-Coulombic interactions ($\chi_s = 0$). In the experimental conditions of the current work, typical values for a κa range from 3 to 10. For large κa , eq 7 is consistent with the linear dependence of σ_{crit} on the square root of ionic strength seen in Figures 4 and 6.

The Locus of Binding. Because of the large molecular volume of the $C_{12}E_6$ polar head groups, the “surface” of the mixed micelles of SDS/ $C_{12}E_6$ is in fact a diffuse region. The DMDAO micelle surface is better defined, and it is of interest to note how the potential decays from this surface at critical conditions. Using the ionic strengths, particle radii (a), and surface potentials measured at critical conditions, we plot the Debye-Hückel screened potentials for a sphere of radius a

$$\psi(x) = \psi_0(a/r) \exp(-\kappa x) \quad (8)$$

for both PAMPS and P(AMPS-NVP) in Figure 8; here $x = r - a$ is the distance from the spherical colloid surface. It is notable that both sets of curves show a common intersection at $x = 6 \pm 0.5$ Å. We suggest that this is the mean position of the bound polyion segments. Thus, the phase boundary may be viewed as the set of experimental conditions which produces a (constant) critical potential at the mean locus of bound polymer units. According to this argument, if the micelle potential probe occupied the same location as the average bound segment, it would report a constant potential at critical conditions. This is the case for PDMDAAC-SDS/ $C_{12}E_6$ with dodecanoic acid as a probe.¹⁵ In this situation, the probe appears to be solubilized in a more distal region, possibly because of its hydrogen bonding to $C_{12}E_6$ head groups, and a constant potential is obtained along the phase boundary.¹⁵ In the case of DMDAO, the surfactant head groups are the probe, and we should not expect that the mean position of the bound segments of the polyion would correspond to this “surface”.

The data that conform best to the simple relationship $\sigma \sim \kappa$ are those obtained with PDMDAAC- $C_{12}E_6$ /SDS, with an HHC probe, at $I > 0.1$ M (see Figure 4); this is likely a consequence of the typically higher ionic strength range used for this system and the larger size of these micelles, as compared to DMDAO. The small Debye length makes the assumptions underlying eq 7 less drastic. With regard to the less impressive fit for the DMDAO results in Figure 6, we should note that the value chosen for the

ionic strength becomes less certain at very low concentrations of added salt because of the difficulty of assessing the contributions of the surfactant and polymers to I . However, increases in the salt concentration in this micellar system are accompanied by drastic changes in micelle dimensions, which would complicate attempts to evaluate treatments such as those described above. Future experiments will focus on systems in which well-defined

colloid geometry can be maintained over a range of σ and I .

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Registry No. DMDAO, 1643-20-5; PAMPS, 55141-01-0; P(AMPS-NVP), 53845-64-0; SDS, 151-21-3; C12E6, 3055-96-7; PDMDAAC, 26062-79-3.

Conformational Characteristics of Short Poly(ethylene oxide) Chains Terminally Attached to a Wall and Free in Aqueous Solution

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Many systems of practical importance contain short polymer chains terminally attached at interfaces. Such systems include sterically stabilized colloids, coated surfaces, compatibility enhancers, micelles, and biological membranes. Although it is generally accepted that for very short chains the well-known polymer scaling laws do not apply, the lower limit of applicability of such laws cannot be easily established a priori. For an aqueous solution of poly(ethylene oxide) (PEO), a system of considerable fundamental and practical importance, we have studied the lower limit of validity of polymer scaling laws for isolated PEO chains free in solution and attached at one end to an inert and impenetrable planar interface (a wall). For this purpose, we have utilized the rotational isomeric state (RIS) model to describe the conformations of PEO chains in water over the temperature range 0–100 °C. The root-mean-square end-to-end distance of free PEO chains ranging in length from 3 to 18 000 bonds was calculated exactly using Flory's serial matrix multiplication method. For the terminally attached PEO chains, this exact method cannot be utilized due to the spatial symmetry breaking induced by the wall. Consequently, we have used a Monte Carlo approach to the RIS model to calculate the root-mean-square end-to-end distance of attached chains ranging in length from 3 to 900 bonds. We find that polymer scaling laws are applicable within an uncertainty of a few percent for fairly short PEO chains. Specifically, the shortest free PEO chain that satisfies scaling with a 2% accuracy has 12 bonds, while the shortest attached chain has 30 bonds. It is also interesting to note that we find a weak temperature variation of the root-mean-square end-to-end distance over the temperature range studied for both free and attached chains. Our results are valid under Θ -solvent conditions, as well as over a range of good-solvent conditions. A discussion of the implications of these new findings for modeling micelles containing alkyl poly(ethylene oxide) (C_iE_j) nonionic surfactants in aqueous solution, as well as for interpreting results of force measurements between two surfaces coated with C_iE_j surfactants and immersed in water, is also presented.

I. Introduction

Many systems of technological importance contain chain polymer molecules attached at one end to an interface.¹ The interface may be a solid surface or the interfacial region between two liquids, between liquid and air, or between melts or solutions of homopolymers. The mechanism of chain attachment depends on the nature of the interface; for example, for solid surfaces, the chain end may be chemically bonded to the surface (end-grafted chain). Depending on the type of interface and method of attachment, a number of important physical systems are encountered. These include the following: (i) colloids sterically stabilized by end-grafted chains, where solid particles are protected against flocculation by attaching grafted chains that have more affinity for the solvent than for each other, (ii) polymeric surfactants, macromolecules composed of a polar end group attached to a hydrocarbon chain that is insoluble in polar solvents, which due to their amphiphilic nature reside preferentially at oil-water interfaces and can therefore be utilized as emulsifiers as well as agents to lower interfacial tensions, and (iii) polymer compatibilizers, macromolecules formed from two dissimilar polymers joined end to end (diblock copolymers), which due to their special chemical architecture adsorb preferentially at interfaces between the constituent polymers and are therefore capable of stabilizing microdomains of one incompatible homopolymer in another.

Most fundamental work in these and related systems has assumed that the polymer chains are sufficiently long to allow the

use of theoretical concepts and methodologies from polymer science, such as polymer scaling laws, which are expected to be valid in the limit of infinitely long chains.² However, it is noteworthy that the systems described in i–iii above often contain relatively short chains. In particular, an important class of systems of this type involves nonionic surfactants of the alkyl poly(ethylene oxide) (C_iE_j) family. The C_iE_j molecules, which are among the most widely studied nonionic surfactants, are linear chains composed of two dissimilar blocks: the hydrophobic tail C_i , an alkane block having i carbon atoms (or $i - 1$ bonds) in the backbone, and the hydrophilic head E_j , a poly(ethylene oxide) (PEO) block having j ethylene oxide units (or $3j$ bonds) in the chain. In many of the investigations involving these surfactants, both i and j are less than 20. In other words, the chains of interest contain less than 100 bonds. For such relatively short chains, the validity of polymer scaling laws is no longer warranted. This observation is particularly relevant for two areas that involve short chains. One is the interpretation of recent experiments involving the measurement³ of forces between two surfaces coated with C_iE_j nonionic surfactants and immersed in aqueous solution, with the E_j chains exposed to the aqueous solvent.^{4,5} The other one is the devel-

(1) For a comprehensive account of theoretical and experimental aspects of long-chain polymers attached at one end to interfaces (polymer brushes), see: Milner, S. T. *Science* **1991**, *251*, 905.

(2) de Gennes, P. J. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(3) For a review on surface force measurements, see: Israelachvili, J.; McGuigan, P. M. *Science* **1988**, *241*, 795.

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