

Complex formation between polyacrylic acid and cationic/nonionic mixed micelles: effect of pH on electrostatic interaction and hydrogen bonding

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Abstract

The interaction of a weak polyacid, sodium polyacrylate (PAA), and cationic mixed micelles of *n*-hexadecyl trimethyl ammonium chloride/*n*-dodecyl hexaoxyethylene glycol monoether (CTAC/C₁₂E₈) was studied by turbidimetric titrations at varying pH, in order to determine the effect of polymer charge. Electrostatically-driven complex formation is controlled by three variables: the polymer linear charge density (ξ), the micelle surface charge density (σ), and the ionic strength (I) or the related Debye–Hückel parameter (κ). In this system, the former two parameters depend, respectively, on α , the degree of ionization of the polymer carboxylic acid groups, and on Y , the micellar mole fraction of ionic surfactant. In 0.10 M salt, the critical mole fraction of CTAC corresponding to the onset of polymer-micelle complex formation, Y_c , varies inversely with pH, as expected, in the range $0.80 < \alpha < 1.0$. At these pH's, $Y_c \times \alpha$ is constant as predicted by our previously proposed equation $\sigma_c \times \xi \times \kappa^{-1} = \text{constant}$, suggesting that the polymer-micelle interaction is predominantly controlled by electrostatic forces. However, at pH 4.0 ($\alpha = 0.10$), Y_c is much smaller than expected. Turbidimetric titration of PAA + C₁₂E₈ with HCl shows complex formation below pH 4.2 even in the absence of CTAC. The concomitant pH increase indicates that the interaction at low pH is dominated by hydrogen bonding. The contribution of H-bonding to PAA–CTAC/C₁₂E₈ complex formation at moderate pH is superimposed on the electrostatically controlled polymer-micelle interaction. An additional factor in PAA–CTAC/C₁₂E₈ complexation is the role of the PAA counterion. Comparison of PAA with poly(acrylamido-2-methylpropane sulfate) in NaCl and in tetramethylammonium chloride indicates that Na⁺ binds to PAA at large α , reducing the effective polymer charge density. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interaction of polyelectrolytes with oppositely charged colloids has attracted considerable interest from both fundamental and industrial points of view. Examples of the relevant phenomena include: (1) nonspecific binding of DNA with

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basic proteins; (2) water purification by colloidal flocculation with polyelectrolytes; (3) immobilization of enzymes in polyelectrolyte complexes; (4) purification of proteins by selective precipitation and coacervation; and (5) phase separation in cosmetics and paint formulations.

Polymer-surfactant systems that are composed of polyelectrolytes and oppositely charged mixed micelles may provide model systems for Coulombic interaction of linear macroions and colloids [1–5]. Theories for the interaction of polyelectrolytes and charged colloids can be evaluated with such systems, since colloid surface charge density is readily altered either by adjusting ionic/nonionic surfactant ratio [1,3,5,6] or – for surfactants which have titratable head groups [2,6,7] – by adjusting the pH.

Intensive studies on polyelectrolytes and oppositely charged mixed micelle systems, such as [8] PDADMAC-SDS/TX100 [1,3,5,7,9,10], PDADMAC-SDS/C₁₂E₆ [2,7], PSS-DTAB/TX100 [6], PSS-DMDAO [6], PAMPS-DMDAO [2], PAMPS-CTAC/C₁₂E₆ [11], have revealed that soluble polyion-micelle complexes exist in certain well-defined regions, and that complexation appears to be a critical phenomenon. Complex formation is dominated by the three fundamental variables; ionic strength (I) (or the related Debye–Hückel parameter, κ), polymer linear charge density (ξ) and micelle surface charge density (σ). The last parameter may be adjusted experimentally in ionic/nonionic mixed micelles via the mole fraction of ionic surfactant, i.e. Y . Many studies demonstrate that Y_c , the mole fraction of ionic surfactant required for complex formation, varies linearly with the square root of the ionic strength ($I^{1/2}$). Since the Debye length (κ^{-1}) varies as $I^{-1/2}$, this dependence suggests that the interaction is predominantly controlled by electrostatic forces. A number of studies [2,6,10–12] have led to an empirical relationship that describes the critical conditions for complexation:

$$\sigma_c \times \xi \times \kappa^{-1} = \text{constant} \quad (1)$$

where σ_c is the critical micelle surface charge density, which is proportional to Y_c , ξ is the linear charge density of polymer, and κ^{-1} , the Debye length, varies with $I^{-1/2}$. This relationship

has been theoretically rationalized by Odijk [13].

In the above examples (PDADMAC, PSS and PAMPS, all strong polyelectrolytes), ξ is constant because the polymer charges are essentially invariable. In contrast, ξ for weak polyions which have titratable acid or base groups, varies continuously as α changes with pH. An earlier study with a weak polybase [14] provided only limited information on the effect of ξ on polyelectrolyte-micelle interactions. Therefore, the interaction between polyacrylic acid (PAA), a well-defined weak polyacid, and CTAC/C₁₂E₈, a cationic/nonionic mixed micelle, was investigated to determine the effect of ξ on complexation. In addition to the electrostatic effects of ξ , we also observe an additional α -dependent H-bonding contribution, giving rise to complex effects of pH on the stability of the polymer–micelle complex.

2. Experimental

2.1. Materials

PAA (MW = 250,000, Aldrich) was neutralized with NaOH, dialyzed and freeze-dried. Concentrations of NaPAA are given as moles of monomer per liter. C₁₂E₈ (Nikko Chemicals) and CTAC (Fluka) were used as received. Milli-Q water was used throughout this work.

2.2. Methods

2.2.1. PAA/CTAC/C₁₂E₈ system

Turbidimetric titrations were carried out at 420 nm using a Brinkman PC800 probe colorimeter equipped with a 1 cm path length fiber optics probe; all solutions were passed through 0.45 μm Alltech filters before titrations. ‘Type I’ turbidimetric titrations [15,16], corresponding to the addition of ionic surfactants to polymer + nonionic surfactant micelle solutions, were performed at $22 \pm 2^\circ\text{C}$ by adding 40 mM CTAC to a mixture of 2.0 mM PAA and 20 mM C₁₂E₈ at a constant ionic strength ($I = 0.10$) and pH; ionic strength and pH were adjusted to desired values with a mixture of NaCl (0.090 M) and buffer salts (pH

9.0, boric acid–NaOH; pH 7.2, NaH_2PO_4 – Na_2HPO_4 ; pH 6.5 and 5.5, MES–NaOH; pH 4.0, acetic acid–Na acetate). The pH drift during titration, monitored by an Orion 811 pH meter equipped with a combination electrode, was within 0.03. All transmittance values were corrected by subtracting the turbidity of a polymer-free blank. The blank-corrected turbidity ($100-T\%$) was plotted vs. Y , the mole fraction of ionic surfactant, defined as $[\text{CTAC}]/([\text{CTAC}] + [\text{C}_{12}\text{E}_8])$.

2.2.2. PAA/ C_{12}E_8 system

‘pH’ turbidimetric titrations, corresponding to the addition of HCl to PAA + C_{12}E_8 solutions, were conducted for 6.9 mM PAA + 20 mM C_{12}E_8 in 0.10 M NaCl at an initial pH 9.0. The turbidity and pH of solution were monitored simultaneously. ‘Type II’ pH titrations, in which pH was monitored upon addition of C_{12}E_8 to a PAA solution, were performed for 6.9 mM PAA with 76 mM C_{12}E_8 in 0.10 M NaCl at an initial pH 4.04.

3. Results and discussion

3.1. PAA/CTAC/ C_{12}E_8 system

Turbidimetric titrations were carried out by adding 40 mM CTAC to 2.0 mM PAA + 20 mM C_{12}E_8 at $I=0.10$ at constant pH. In Fig. 1, the turbidity (reported as $100\% T$) is plotted against Y , the mole fraction of CTAC in CTAC/ C_{12}E_8 mixed micelles. For pH 9.0, the turbidity begins to increase at $Y=0.18$, followed by abrupt phase separation at $Y=0.24$. These observations agree with those of previous studies on a number of similar polyelectrolyte-mixed micelle systems [1–7,9–11], which also show two critical values of Y . The effects cannot be attributed to any significant degree to changes in micelle size with Y , since the size of $\text{C}_{12}\text{E}_6/\text{CTAC}$ micelles in the absence of polymers has been found by QELS to be 7.5 ± 0.2 nm, independent of Y in the range $0.05 < Y < 0.25$ [17]. The first appearance of turbidity in excess of that of the polymer-free solutions (Y_c) corresponds to the onset of polymer-micelle com-

plex formation; and a more abrupt and dramatic turbidity change (Y_p) corresponds to macroscopic phase separation. Since the phenomena corresponding to this phase separation at Y_p , which may include charge neutralization and stoichiometric effects, are not well-understood, we mainly discuss Y_c in this report. Y_c appears to shift systematically from 0.18 to 0.21–0.23 as the pH decreases from 9.0 to 7.2–6.5, respectively. The

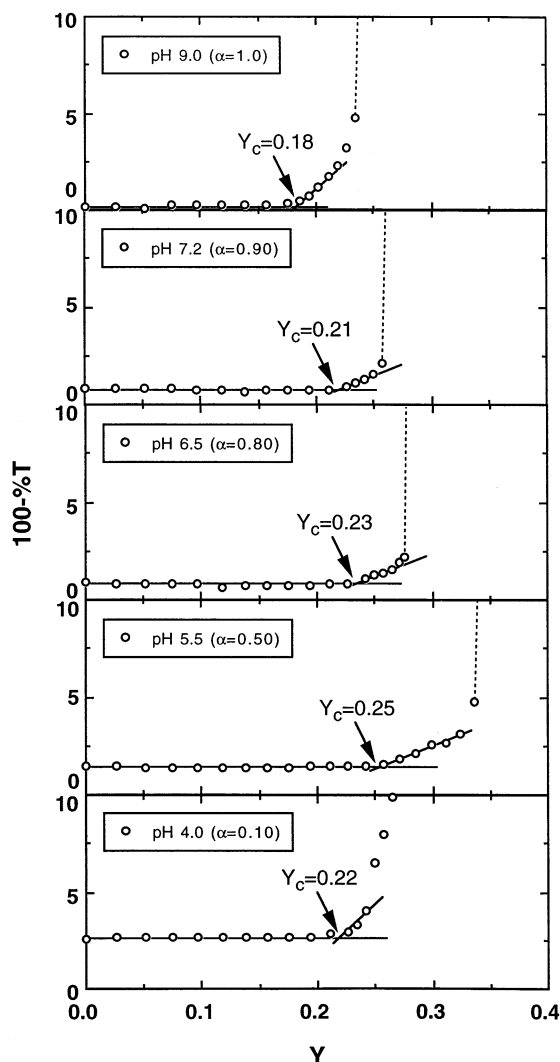


Fig. 1. ‘Type I’ turbidimetric titrations (addition of CTAC to a mixture of PAA and C_{12}E_8 at constant ionic strength) at pH 9.0, 7.2, 6.5, 5.5 and 4.0, for 2.0 mM PAA + 20 mM C_{12}E_8 titrated with 40 mM CTAC in $I=0.10$. Y is the mole fraction of CTAC in the mixed micelle.

Table 1

Effect of polyacid dissociation degree on Y_c for PAA/CTA/C12E8 in $I = 0.10$

pH	α	Y_c	$Y_c \times \alpha$
9.0	1.0	0.18	0.18
7.2	0.90	0.21	0.19
6.5	0.80	0.23	0.18
5.5	0.50	0.25	0.13
4.0	0.10	0.22	0.02

dependence of the degree of dissociation (α) on pH for PAA [18] indicates how the linear charge density (ξ) depends on pH. The inverse dependence of Y_c on pH is consistent with the interaction of a strong polyelectrolyte copolymer and mixed micelles; poly(AMPS-co-vinylpyrrolidone) copolymer (low ξ) showed larger Y_c than PAMPS homopolymer (high ξ) [2].

If Y_c corresponds to the minimum surface charge density (σ_c) of a mixed micelle required for polymer-micelle complex formation, it should—according to Eq. (1)—increase with decreasing ξ , which varies linearly with α . Thus, since Y_c is proportional to σ_c , and α to ξ , Eq. (1) comes at fixed I :

$$Y_c \times \alpha = \text{constant} \quad (2)$$

Consequently, Y_c should be inversely proportional to α . pH, α , and Y_c determined from Fig. 1 are summarized in Table 1. $Y_c \times \alpha$ is indeed constant as predicted in the range $9.0 > \text{pH} > 6.5$; however, Y_c is unexpectedly small at pH 4.0–5.5. As seen from the turbidity titration curves in Fig. 1, the initial turbidity (at $Y=0$) for low pH is significantly larger than that at pH 9.0, indicating that PAA-micelle complex formation occurs even without CTAC. Thus, the meaning of the measured ' Y_c ' at low pH is somewhat different, and corresponds to the onset of 'charge-induced' complexation. The small Y_c and large turbidity at $Y=0$ indicate that a non-electrostatic attractive force influences the interaction at low pH. This is consistent with Saito's report that H-bonding controls the interaction between PAA and polyoxyethylene (POE) type nonionic surfactant at acidic conditions [19–21].

3.2. PAA–C₁₂E₈ system

To confirm the effect of pH on complexation of PAA–C₁₂E₈ (CTAC-free), 'pH' turbidimetric titrations were conducted by adding HCl to 6.9 mM PAA + 20 mM C₁₂E₈ in 0.10 M NaCl at an initial pH 9.0. As shown in Fig. 2, upon decreasing pH, the turbidity increases abruptly at pH 4.2, indicating complex formation below a critical pH (pH_c 4.2). This PAA–C₁₂E₈ complex formation appears to be reversible; addition of NaOH to the turbid solution causes the turbidity to recover to its prior value. At pH_c , α for PAA in 0.10 M NaCl is 0.15; Saito reported that the interaction occurs at $\alpha < 0.20$ in pure water [19].

A 'Type II' pH titration was performed by monitoring the pH during the addition of 76 mM C₁₂E₈ to 6.9 mM PAA in 0.10 M NaCl at an initial pH 4.04. Although complex formation should occur at this pH (just below pH_c 4.2), the solution remains clear while the pH increases. In Fig. 3, the result is plotted as $\Delta[\text{H}^+]$ against $[\text{C}_{12}\text{E}_8]$. The decrease in $[\text{H}^+]$ upon addition of C₁₂E₈ agrees with Saito's observations [19], and suggests that some of the carboxyl group protons are fixed due to H-bonding between PAA and the surfactant, which stabilizes the undissociated form of carboxyl groups.

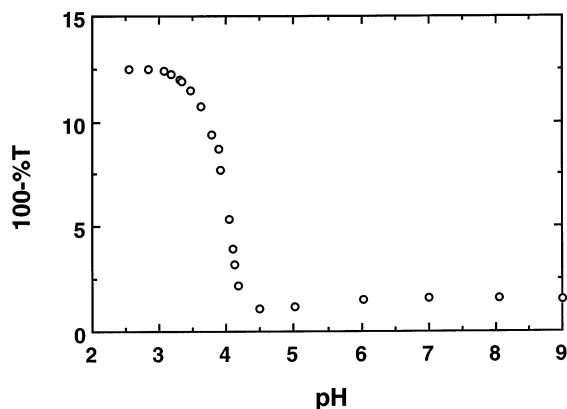


Fig. 2. 'pH' turbidimetric titration (addition of HCl to a mixture of PAA and C₁₂E₈ at constant ionic strength) for 6.9 mM PAA + 20 mM C₁₂E₈ in 0.10 M NaCl at initial pH 9.0.

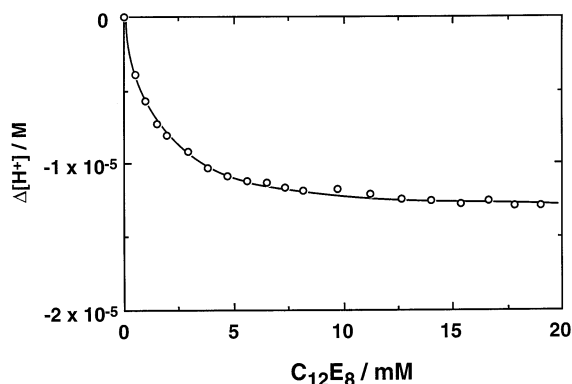


Fig. 3. ‘Type II’ pH titration (addition of $C_{12}E_8$ to PAA at a constant ionic strength) for 6.9 mM PAA with 76 mM $C_{12}E_8$ in 0.10 M NaCl at initial pH 4.04.

3.3. Phase diagram for PAA/CTAC/ $C_{12}E_8$ system

The dependence of critical Y 's (Y_c and Y_p) on pH for PAA/CTAC/ $C_{12}E_8$ is shown in Fig. 4. Both Y_c and Y_p increase with decreasing pH, indicating the electrostatic interaction is weakened by decreasing α ($\propto \zeta$). For ‘Type I’ turbidity titration at pH 4.0 ($\alpha = 0.1$), turbidity changes gradually above Y_c , and requires 15–30 min to reach a stable value, compared to the other pH's (usually within 1–2 min). Furthermore, an abrupt

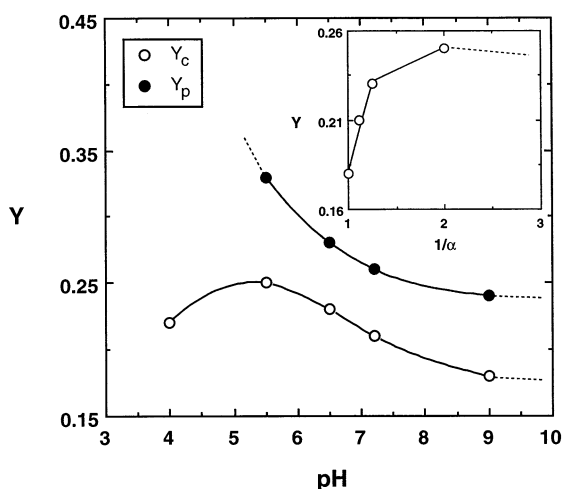


Fig. 4. Dependence of critical Y 's (Y_c and Y_p) on pH for PAA/CTAC/ $C_{12}E_8$ in $I = 0.10$. Insert: Y_c versus $1/\alpha$.

turbidity change, corresponding to a macroscopic phase separation, is not observed at pH 4.0, so that Y_p is not determined in this case.

The dependence of Y_c on $1/\alpha$ is shown in the insert of Fig. 4. At large α , Y_c may change linearly with $1/\alpha$ as predicted by Eq. (2). Y_c at lower α is smaller than expected, presumably due to the additional H-bonding contribution. Although ‘pH’ turbidimetric (Fig. 2) and ‘Type II’ pH (Fig. 3) titrations reveal that $C_{12}E_8$ micelles interact with PAA through H-bonding at pH < 4.2, Y_c for pH 5.5 is smaller than expected, suggesting that H-bonding affects Y_c even at higher pH. $C_{12}E_8$ micelles may indeed bind to PAA without CTAC, but turbidity does not change until Y reaches a critical value (see Fig. 1). We thus observe both electrostatic and H-bonding interaction for PAA and CTAC/ $C_{12}E_8$. However, the interrelationship of the two effects is not well understood at present.

Since Y_c is inversely proportional to α , varying α in the high α range produces only small effects on Y_c . Thus, decreasing α from 1.0 to 0.80 yields only a relatively small increase in Y_c (28%). Changes in Y_c are difficult to monitor precisely in such a narrow α region. Since $\sigma_c \propto Y_c$, $\zeta \propto \alpha$, and $\kappa^{-1} \propto I^{-1/2}$, we obtain from Eq. (1):

$$Y_c \times \alpha = \text{constant} \times I^{1/2} \quad (3)$$

so that

$$dY_c/d(1/\alpha) \propto I^{1/2} \quad (4)$$

Therefore, we may increase the dependence of Y_c on α by increasing the ionic strength. However, when we carried out experiments at $I = 0.50$, we found, rather remarkably, no turbidity change or phase separation. It was equally surprising to observe that Y_c appeared to be independent of pH at $I = 0.20$, in the range $0.65 < \alpha < 1.0$.

The constancy of Y_c with respect to α was unexpected, inasmuch as it suggests that σ_c is independent of ζ , contradicting Eq. (1). If Eq. (1) is correct, this result suggests that ζ does not depend on α in the expected way for PAA. One origin of such an effect could be local polarization of charges in partially ionized PAA. Since the charge on each monomer unit of PAA is labile, the local polymer linear charge density could ex-

Table 2
Effect of polymer counterion on Y_c for PAA and PAMPS at pH 9.0

Salt	Ionic strength	Y_c	
		PAA	PAMPS
NaCl	0.10	0.18	0.10
	0.20	0.31	–
TMAC	0.10	–	–
	0.20	0.17	0.17

ceed the value corresponding to the average degree of dissociation. The local charge distribution of partially ionized PAA could therefore adjust upon binding to an oppositely charged micelle. The effective ξ of this ‘annealed’ PAA might not be a simple linear function of α . To test this hypothesis, ‘Type I’ turbidity titrations were performed in which we compared PAA at pH 6.0 ($\alpha = 0.70$) (‘annealed’) to poly(acrylate-co-acrylamide) (70/30) at pH 9.0 (‘quenched’), in $I = 0.20$ M NaCl. Since the charge distribution on PAA-co-AAm at pH = 9.0 is fixed and cannot fluctuate, it was expected to show a larger Y_c than for PAA, even though the formal charge densities are the same. PAA-co-AAm (70/30) indeed showed a larger Y_c than 70% neutralized PAA, namely $Y_c = 0.34$ versus 0.31. However, this effect is too small to account for the invariance of Y_c at $\alpha > 0.65$.

Deviation between ξ_{eff} and the apparent value based on α could also arise from counterion binding. Since the bulky cation tetramethylammonium shows little specific ion binding [22], turbidimetric titrations were conducted at pH 9.0, in NaCl and tetramethylammonium chloride (TMAC), for NaPAA and PAMPS, two polyions with identical structural charge densities. The results of this preliminary study are shown in Table 2. Y_c for NaPAA was found to be 80% larger than that for PAMPS, indicating that the effective value of ξ is smaller for NaPAA. On the other hand, Y_c values for the two polymers were equal in tetramethylammonium chloride (TMAC). These results suggest that ξ_{eff} for NaPAA is reduced as a consequence of the binding of Na^+ . The stronger

binding to PAA of Na^+ relative to TMA^+ is consistent with the results of potentiometric studies [22] for other polycarboxylic acids. PAMPS, with bulky, low charge density sulfonate groups, appears to be insensitive to this effect. The result of Na^+ binding to PAA is thus a ‘leveling’ of ξ_{eff} so that no effect of α can be seen.

4. Conclusions

We observed that $Y_c \times \alpha$, equivalent to $\sigma_c \cdot \xi$, is constant for PAA-CTAC/ C_{12}E_8 interaction under certain conditions (large α , low I) in a manner consistent with Eq. (1): $\sigma_c \cdot \xi \cdot \kappa^{-1} = \text{constant}$. However, H-bonding between undissociated carboxyl groups of PAA and POE of C_{12}E_8 contributes to the binding affinity at low α , making it difficult to separately determine the electrostatically controlled interaction. At high ionic strength and α , the effect of α on Y_c appears to vanish. Comparison of PAA with PAMPS in NaCl and in TMAC shows that this result arises from the binding of Na^+ to PAA.

Acknowledgements

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- [8] Abbreviations: PDADMAC, poly(diallyldimethylammonium chloride); PSS, poly(styrenesulfonate); PAMPS, poly(acrylamido-2-methylpropane sulfonate); SDS, sodium dodecyl sulfate; C₁₂E₆, dodecylhexaoxyethylene glycol monoether; TX100, Triton X-100; DTAB, dodecyltrimethylammonium bromide; DMDAO, dimethyldodecylamine oxide.
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