

Reprinted from *LANGMUIR*, 1993, 9.  
Copyright © 1993 by the American Chemical Society and reprinted by permission of the copyright owner.

# Interaction of Tetradecyltrimethylammonium Bromide with Poly(acrylic acid) and Poly(methacrylic acid). Effect of Charge Density

J. J. Kiefer and P. Somasundaran

*Langmuir Center for Colloids and Interfaces, Columbia University, New York, New York 10027*

K. P. Ananthapadmanabhan\*

*Unilever Research, U.S., Edgewater, New Jersey 07020*

*Received April 1, 1992. In Final Form: March 10, 1993*

The effect of polymer charge density on the interaction of tetradecyltrimethylammonium bromide (TTAB) with poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) has been investigated using a surfactant-sensitive solid-state membrane electrode. The experimental results indicate that the interaction with PAA begins at about the same equilibrium TTAB concentration when the degree of ionization ( $i$ ) of the polymer is greater than about 0.4. This value, according to Manning's counterion condensation theory, corresponds to the critical degree of ionization for PAA above which the effective charge density of the polymer is constant. The salt, NaBr, because of its high concentration in the system ( $10^{-2}$  M), essentially controls charge density of the polymer, and this can account for the absence of any measurable variation in the onset of binding above an ionization of 0.4. Surprisingly, when  $i < i_c (=0.4)$ , the onset of TTAB binding to PAA and PMA shifts to lower free TTAB concentrations. The results suggest that the onset of binding is significantly influenced by changes in polymer conformation and possibly hydrophobicity of the backbone that occur at these low degrees of ionization. In the plateau region of the binding isotherm, PAA and PMA exhibit opposite behavior. The plateau binding fraction for PAA at degrees of ionization ( $i$ ) of 0.10, 0.26, and 0.50 exceeds 1.0, the expected value required for charge neutralization. In contrast PMA at  $i = 0.26$  exhibits a plateau binding fraction of 0.5, much less than that required for charge neutralization. The low plateau value for PMA at low degree of ionization is thought to result from the highly coiled nature of PMA which possibly renders a substantial fraction of the ionized carboxyl groups unavailable for interaction with the surfactant. The sharp increase beyond the plateau is attributed to surfactant-induced opening of the coiled PMA.

## Introduction

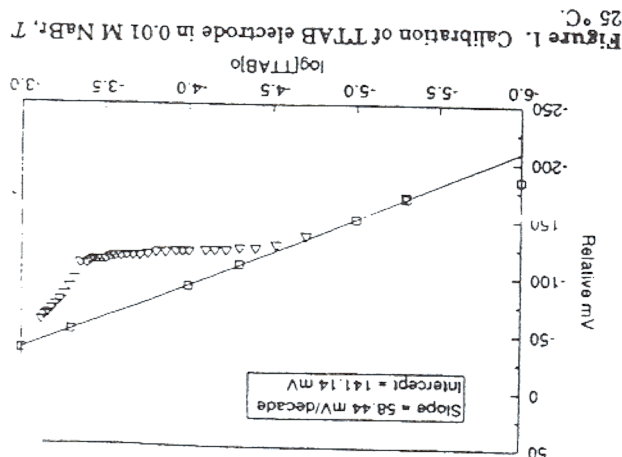
Complexation between polymers and surfactants has been studied for many years. Early work focused on the interaction of synthetic surfactants with proteins in solution. Later work focused on the interaction of anionic surfactants with uncharged water-soluble polymers such as poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP). The interaction of anionic surfactants with uncharged polymers occurs as bulk surfactant concentration approaches the critical micelle concentration (cmc). Recently many studies have also been conducted on interactions of ionic polymers with charged surfactants.<sup>1-3</sup> Interactions in these systems are predominantly electrostatic and are strong compared to those in uncharged polymer systems due to the presence of long range electrical forces and occur at surfactant concentrations much less than the cmc. Initial work in this area focused on the interaction of cationic cellulose derivatives with anionic surfactants such as sodium dodecyl sulfate (SDS) using techniques such as surface tension, dye solubilization, and fluorescence spectroscopy.<sup>3-5</sup> Similar systems have also

been studied using various NMR techniques.<sup>6</sup>

Binding of ionic surfactants to oppositely charged polymers has been studied by a variety of techniques such as equilibrium dialysis, conductivity and potentiometry, etc.<sup>2</sup> Potentiometry employing surfactant-sensitive membrane electrodes is the most direct method for determining the binding of a surfactant to a polymer. Kwak and co-workers<sup>7-12</sup> and others<sup>13,14</sup> have employed these surfactant-sensitive electrodes to study the effect of ionic strength, multivalent cations, surfactant chain length, polymer structure, and temperature on the binding of cationic surfactants to anionic polyelectrolytes. These studies show that the binding is highly cooperative and is

- (1) Goddard, E. D. *Colloids Surf.* 1986, 19, 255-300.
- (2) Goddard, E. D. *Colloids Surf.* 1986, 19, 301-329.
- (3) Goddard, E. D.; Hannan, R. B. *J. Colloid Interface Sci.* 1976, 55, 73-79.
- (4) Leung, P. S.; Goddard, E. D. *Colloids Surf.* 1985, 13, 47-62.
- (5) Ananthapadmanabhan, K. P.; Leung, P. S.; Goddard, E. D. *Colloids Surf.* 1985, 13, 63-72.

- (6) Lindman, B.; Soderman, O.; Wennerstrom, H., "NMR Studies of Surfactant Systems" In *Surfactant Solutions: New Methods of Investigation*; Surfactant Science Series; Zana, R., Ed.; Marcel Dekker: New York, Vol. 22, 1984; p 295.
- (7) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* 1982, 86, 3866-3870.
- (8) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* 1983, 87, 506-509.
- (9) Malikova, A.; Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* 1984, 88, 1930-1933.
- (10) Santerre, J.; Hayakawa, K.; Kwak, J. C. T. *Colloids Surf.* 1985, 13, 35-45.
- (11) Hayakawa, K.; Santerre, J.; Kwak, J. C. T. *Macromolecules* 1985, 16, 1642-1645.
- (12) Shimizu, T.; Seki, M.; Kwak, J. C. T. *Colloids Surf.* 1986, 20, 289-301.
- (13) Shirahama, K.; Yuasa, H.; Sugimoto, S. *Bull. Chem. Soc. Jpn.* 1984, 54, 375-377.
- (14) Shirahama, K.; Tashiro, M. *Bull. Chem. Soc. Jpn.* 1984, 57, 377-380.



### Materials and Methods

Samples of high molecular weight PAA and PMA were obtained as the acid, in powder form, from Scientific Polymer Products and used as received. Stock solutions of all polymers were prepared by dissolving the solid acid in distilled water. The concentration of the polymer in solution was determined by titration with NaOH in 0.01 M NaBr and expressed as equivalents of monomeric acid.

PAA and PMA were characterized by intrinsic viscosity using a Cannon Ubbelohde four-bulb shear dilution capillary viscometer. The viscosity-average molecular weight can be calculated from the Mark-Houwink equation

$$[\eta] = K(M_v)^n \quad (1)$$

The values of  $K$  and  $n$  along with the appropriate solvent conditions are given in ref 19. The viscosity-average molecular weight for PAA was found to be 598 000 and was determined in 2 M NaOH. The intrinsic viscosity for PMA was determined in dilute HCl and methanol. The viscosity-average molecular weight obtained in each solvent was averaged to yield 257 000. Tetradecyltrimethylammonium bromide (TTAB), obtained from Sigma Chemical Co., was recrystallized twice from acetone and dried overnight at 30 °C under vacuum. Sodium dodecyl sulfate obtained also from Sigma Chemical Co. was used as received.

Free surfactant concentrations were determined potentiometrically using a surfactant-sensitive membrane electrode prepared according to the procedure given by Kwik.<sup>2</sup> Standardization of the electrode was accomplished by presoaking the electrode in 10<sup>-4</sup> M TTAB for approximately 2 h and then soaking in distilled water for about 10 min. The electrode was then placed in standard TTAB solutions (10<sup>-4</sup> to 10<sup>-2</sup> M TTAB) for 2 min and the millivolt reading for each standard was recorded and a calibration curve constructed.

In general the electrode calibration is very reproducible. However, directional drift in the calibration curve was observed. This caused the calibration curve to shift (+2 mV) along the potential axis while maintaining an essentially constant slope. The effect of this drift on the experiment was minimized by calibration of the electrode before and after each titration. The millivolt readings were then averaged and a single calibration curve was constructed. A typical surfactant electrode calibration curve is shown in Figure 1. As can be seen, the plot is linear over several orders of TTAB concentration indicating Nernstian behavior with a slope of 58.4 mV/decade.

Binding isotherms were obtained by titrating the polymer solution with standard TTAB solutions in a thermostated glass beaker maintained at 25 ± 0.1 °C. The potential relative to a saturated calomel reference (Fisher Scientific) was recorded using a Kyoto Electronics Model AT-210 autotitrator equipped with a standard titration preamplifier and Model AT-118 autopotision

shifted to higher free surfactant concentration by the presence of univalent salts. Multivalent cations were found to compete with surfactant for binding sites on these polymers and in some cases suppressed the binding. The effect of temperature on the binding isotherm was small with the standard enthalpy of binding decreasing only slightly with an increase in temperature. Studies on binding of cationic surfactants to copolymers containing several chemically different ionizable groups were found to yield binding isotherms with distinct portions corresponding to different binding sites.

The effect of charge density on the interaction of charged surfactants with oppositely charged polyelectrolytes has been studied by Kwik<sup>2</sup> by comparing the binding isotherms of cationic surfactant on several anionic polyelectrolytes such as poly(acrylic acid), dextran sulfate, poly(vinyl sulfate), poly(styrenesulfonate), carboxymethylcellulose, alginate, and pectate. Their results did not show any strong correlation between the charge density of the polymer and the binding isotherm. They correctly pointed out the difficulties in isolating the charge effects from those due to differences in molecular weight, chain flexibility, and chemical nature of the ionizable group. An alternative method to study this effect is by varying the charge density of the polymer by changing the solution pH. Such an approach has been used by Shimizu et al. in their study of the binding of dodecylpyridinium chloride and dodecyltrimethylammonium chloride with copolymers of maleic acid with ethylene, ethyl vinyl ether, styrene, and indene. Interestingly, some of their systems showed stronger interactions at lower charge density. They also observed two-step binding isotherms for the more hydrophobic copolymers. The first rise was attributed to binding to sites with both hydrophobic and electrostatic interactions and the second only to electrostatic interactions. While these results are interesting and informative, effects appear to be influenced markedly by the strong hydrophobic nature of these polymers. In this regard, note that the effect of the charge density of a relatively hydrophilic polymer such as poly(acrylic acid) or of a moderately hydrophobic polymer such as poly(methacrylic acid) is not well understood. In this case, the pH variation method yields a way to isolate the effect of charge density from the effect of the chemical structure. In this work the effect of polymer charge density on the binding of tetradecyltrimethylammonium bromide (TTAB) to poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) is determined by varying the pH. Studies incorporating PMA provide the opportunity to understand the effect of polymer conformation on surfactant binding. Using potentiometric analysis<sup>15,16</sup> and fluorescence spectroscopy,<sup>17,18</sup> PMA has been shown to undergo marked conformational changes as a function of charge density. These experiments show that PMA is in a highly compact form at low charge densities and opens to an extended coil at high charge density. The compact structure of PMA at low charge density is thought to result from the hydrophobic interactions between the adjacent methyl groups on the PMA backbone. In contrast, PAA adopts a random coil conformation at low charge density and an extended coil at high charge density. The effect of these differences on their interaction with TTAB was investigated in this study.

- (15) Chidambaram, S.; Gundiah, S. *Makromol. Chem.* 1985, 186, 223.
- (16) Marinsky, J. J. *Phys. Chem.* 1985, 19 (24), 5294-5302.
- (17) Chu, D.; Thomas, J. K. *J. Am. Chem. Soc.* 1986, 108, 6270-6276.
- (18) Oles, A. F.; Thomas, J. K. *Macromolecules* 1989, 22, 1165-1169.

- (19) *Polymer Handbook*, 3rd ed.; Bandrup, J., Immergut, E. H., Eds.; Wiley Interscience: New York, 1969.
- (20) Somasundaram, P. *J. Phys. Chem.* 1966, 70, 90.

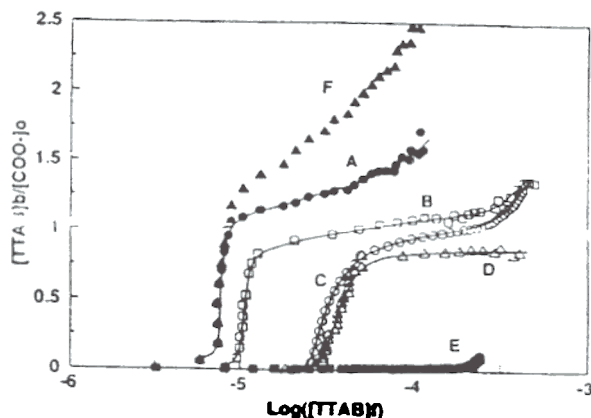


Figure 2. Effect of polymer charge density on TTAB binding to PAA, in 0.01 M NaBr:  $T = 25^\circ\text{C}$ ;  $[\text{PAA}] = 5.0 \times 10^{-4}$  equiv L $^{-1}$ ; curve A,  $i = 0.14$ ; curve B,  $i = 0.26$ ; curve C,  $i = 0.50$ ; curve D,  $i = 1.0$ ; curve E,  $i = 0$ ; curve F, isotherm without corrections for pH at  $i = 0.14$ . (Curve A represents the corresponding corrected isotherm at  $i = 0.14$ .)

buret. The standard 0.01 M TTAB titrant was delivered in either 0.1- or 0.2-mL increments. The resulting potential was recorded 2 min after each incremental addition of titrant. Free surfactant concentrations were estimated using the millivolt versus concentration calibration curve.

### Results and Discussion

**Surfactant Binding Isotherms.** The activity of surfactant ions in the presence of polymer was measured with the surfactant-sensitive electrode as discussed above, and the amount of surfactant associated with the polymer was estimated by comparing the activity to that in a polymer-free solution containing an equivalent amount of total surfactant. The binding isotherm is represented as the fraction of available sites occupied by the surfactant as a function of free surfactant concentration and is calculated using the expression given by

$$\beta = \frac{[\text{TTAB}]_0 - [\text{TTAB}]_f}{[\text{COO-}]_0} \quad (2)$$

where  $[\text{TTAB}]_0$  is the concentration of added surfactant,  $[\text{COO-}]_0$  is the concentration of ionized carboxyl groups, and  $[\text{TTAB}]_f$  is the free surfactant concentration. Note that in these calculations the activity is taken to be equal to the concentration, and this is justified since the electrode measurements in surfactant solutions show Nernstian behavior over the wide range of concentrations employed in the present study.

### Effect of the Degree of Ionization on TTAB Binding

The effect of charge density was studied by varying the degree of ionization,  $i$ , of the polymer with NaOH. The degree of ionization can be taken as equivalent to the degree of neutralization,  $\alpha$ , if  $\alpha$  is in the range of 0.15–0.85. For the case of fully neutralized PAA, i.e.  $\alpha = 1.0$ , the degree of ionization is somewhat less than 1.0. In fact, it can be shown that  $i$  is about 0.98 when  $\alpha = 1.0$ . Therefore, in this study  $\alpha$  is assumed to be equal to the degree of ionization,  $i$ .

**PAA-TTAB System.** The binding isotherms of TTAB to PAA obtained at  $i = 0.10, 0.26, 0.50$  and  $1.00$  in 0.01 M NaBr at  $25^\circ\text{C}$  are given in Figure 2. In addition, curve E of figure 2 represents the binding isotherm in 0.01 M HBr which corresponds to a degree of ionization of zero. The isotherms exhibit the typical sigmoidal shape associated with cooperative phenomena except for the case

when  $i = 0$ . Several special features become apparent upon comparison of the binding isotherms:

(a) The onset of cooperative binding at  $i = 0.50$  and  $1.0$  occurs almost at the same free TTAB concentration of about  $2 \times 10^{-5}$  M.

(b) The onset of cooperative binding at  $i = 0.10$  and  $0.26$  occurs at a lower free surfactant concentration than at  $i = 0.50$  and  $1.0$ .

(c) When  $i = 0$ , there is little or no interaction between TTAB and PAA until the TTAB concentration reaches about  $2 \times 10^{-4}$  M.

(d) When the degree of ionization is  $0.10, 0.26$ , and  $0.50$ , the value of  $\beta$  is found to exceed unity at high surfactant concentration.

(e) For the case of  $i = 1$ , the plateau  $\beta$  value does not exceed unity and does not exhibit any increase in the range of surfactant concentration studied once the plateau value is reached.

One would normally expect the interaction between a polyelectrolyte and an oppositely charged surfactant to be stronger at a higher polymer charge density. The present result appears to contradict this notion but appears to be similar to some of the results reported by Shimizu et al.<sup>12</sup> for the binding of cationic surfactants with hydrophobic copolymers of maleic acid with styrene, ethyl vinyl ether, and indene. Interestingly, our isotherms for PAA at  $i = 0.5$  and  $1.0$  almost coincide with each other, suggesting that the effective charge density of PAA when  $i = 0.50$  and  $1.0$  is about the same. This apparently anomalous behavior is thought to be due to a combination of two effects, namely Manning's counterion condensation effects<sup>21,22</sup> which reduce the effective charge density of the polymer to a constant value above the critical charge density ( $i_c$ ) and the presence of an indifferent electrolyte, NaBr, at such high levels such that it essentially controls the condensation effects. Manning's theory of polyelectrolyte solutions<sup>21,22</sup> states for "dilute solutions, sufficiently many counterions will condense on the polyion to lower the charge-density parameter,  $\xi$ , to the value one"<sup>21</sup> for a 1:1 electrolyte. The remaining uncondensed counterions can be treated according to the Debye-Huckel theory and considered to interact with a polyion of effective charge density,  $\xi^{-1}$ . The charge density parameter is defined as

$$\xi = e^2/b\epsilon kT \quad (3)$$

where  $e$  is the protonic charge,  $b$  is the linear charge spacing,  $\epsilon$  the solvent dielectric constant,  $k$  the Boltzmann constant, and  $T$  the absolute temperature. Using the critical condition,  $\xi = 1.0$ , a critical linear charge spacing,  $b_c$ , can be calculated. On the basis of the above reasoning, we expect for a linear polyelectrolyte with linear charge spacing greater than  $b_c$  counterions not to strongly bind to the polymer backbone. In water at  $25^\circ\text{C}$ ,  $b_c$  is found to be  $7.20 \text{ \AA}$  charge. The linear charge spacing,  $b$ , of PAA can be varied with the degree of ionization,  $i$ , and can be expressed as

$$b(i) = b_0/i \quad (4)$$

where  $b_0$  is the intrinsic charge spacing between carboxyl groups on adjacent monomer units. The value of  $b_0$  is taken to be  $2.76 \text{ \AA}$  from measurements on CPK® space filling models. Substitution of  $7.20 \text{ \AA}$  for  $b(i_c)$  into eq 4 gives  $i_c = 0.38$ . Now, based on Manning's theory, the effective polymer charge density will remain constant for  $i \geq i_c$ . In the present system, the counterions will be made up of both the  $\text{Na}^+$  ions and the surfactant cations. Note

(21) Manning, G. S. *J. Chem. Phys.* 1969, 51, 924.

(22) Manning, G. S. *Q. Rev. Biophys.* 1978, 2, 179.



that the binding isotherms were determined in  $10^{-2}$  M NaBr solutions. Under these conditions, the concentration of the salt is about 2 to 3 orders of magnitude higher than that of the surfactant. Since electrostatics will not distinguish between the  $\text{Na}^+$  ions and the surfactant cations in the preassociative interaction region, the proportion of the surfactant to  $\text{Na}^+$  in the condensed layer can be expected to be essentially the same as in the bulk solution. Thus, the expected differences in the concentration of TTAB<sup>+</sup> in the bulk solution, because of its cocondensation, are  $1 \times 10^{-7}$  and  $7 \times 10^{-7}$  M at ionization values 0.5 and 1.0, respectively. This difference is relatively small compared to the initial concentration in the system and therefore the onset of binding appears to be at about the same initial concentration. This is equivalent to stating that the charge density is controlled by the  $\text{Na}^+$  ions and is invariant for ionization values above about an ionization of 0.4.

At low degrees of ionization, less than  $i_c$ , the onset of binding occurs at lower free surfactant concentration than those at  $i \geq i_c$ . We attribute this to conformational changes in the polymer coil when the degree of ionization is below the critical value and to the role of polymer conformation on binding. This hypothesis is supported by fluorescence results obtained by Turro and Arora<sup>23</sup> on pyrene labeled PAA. Their results show a marked increase in the pyrene monomer to excimer ( $I_m/I_e$ ) ratio over a pH range from 5.5 to 6.5. They interpret the increase in  $I_m/I_e$  as an uncoiling of the polymer chain with increasing ionization. Above and below this pH range the value of  $I_m/I_e$  remained essentially constant. The pH range over which PAA significantly changes conformation, corresponds to the region of the critical degree of ionization  $i_c$  for PAA. Note that in addition to coiling, the hydrophobicity of the polymer also may increase with decrease in the charge density. This may also be responsible for the observed increase in binding with decrease in charge density below  $i_c$ .

Interestingly when the degree of ionization is zero (curve E on Figure 2) there is little or no interaction of TTAB with PAA until the surfactant concentration reaches about  $2 \times 10^{-4}$  M. At this point an increase in the isotherm is observed. This rise occurs at about the same TTAB concentration as the marked rise beyond the plateau region for  $i = 0.26$  and 0.50. The position of the isotherm at  $i = 0.0$  suggests that a small negative charge on the polymer is required to attract TTAB ions to the vicinity of the polymer coil. Evidently, conformational factors and possible favorable changes in the backbone hydrophobicity, but without any electrostatic interaction, do not lead to enhanced binding. Interestingly, the onset of binding at  $i = 0$  is still well below the cmc of TTAB in 0.01 M NaBr. This is reminiscent of the behavior observed for charged surfactant-nonionic polymer systems.

As mentioned earlier, another interesting feature of the binding isotherm for  $i$  values of 0.10, 0.26, and 0.5 is the  $\beta$  value above unity. Similar results have been reported by Shimizu et al. for the binding of dodecylpyridinium and dodecyltrimethylammonium cations on hydrophobic modified alternating copolymers of maleic acid.<sup>12</sup> A binding fraction greater than 1 means more binding than that required for charge neutralization. This can be the result of a number of phenomena. For example, TTAB can displace protons from the polymer and increase the number of available binding sites beyond that calculated based on the degree of ionization. However, the fact that pH remained essentially constant for  $i = 0.26$  along the

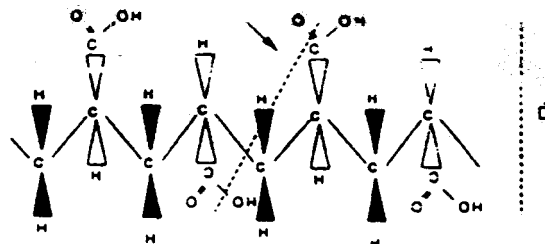


Figure 3. Schematic representation of PAA chain.

binding isotherm rules out this possibility for this case. Similarly, the pH was found not to change along the isotherm for  $i$  values greater than 0.26. However, a change in pH was observed during addition of TTAB to PAA with a degree of ionization of 0.10. For example, a noted pH change from 4.5 to 4.0 corresponded to a change in the degree of ionization of the polymer from 0.10 to 0.18. This change in pH of the solution was used to calculate the fraction of additional carboxyl groups ionized at each addition of titrant during the experiment. It was assumed in this calculation that the protons released during the titration were due to ionization of the PAA which resulted in a decrease in the solution pH. In this manner a correction to the binding isotherm was calculated. The corrected isotherm is curve A in Figure 2. It is apparent that even when the correction is applied, the binding isotherm is significantly above unity. On the basis of these results, we conclude that the rise above unity is not due to ionization of PAA as a result of TTAB binding.

Assuming that the charge on the polymer is completely neutralized by the cationic surfactant at  $\beta = 1.0$ , the major driving force for the continued uptake of surfactant by the polymer has to be hydrophobic interaction. This could be due to incorporation of more surfactant into existing polymer-surfactant aggregates or the formation of a second layer as has been shown to occur at the solid-liquid interface.<sup>20</sup>

It is to be noted that the solution did develop a slight blue tinge at the beginning of the plateau region. Upon further surfactant addition, marked turbidity developed and the solution remained turbid in the entire region beyond the plateau. The possibility of the precipitate affecting the performance of the electrode was checked by restandardization of the electrode. The electrical behavior remained normal after exposure to a turbid solution. Furthermore, the rise in the binding isotherm is reproducible. Also such a rise in the binding isotherm was not observed for PAA when  $i = 1.0$  even though the solution was turbid. Therefore, it can be concluded that the sharp rise in the isotherm beyond the plateau is a real phenomenon.

In contrast to the results obtained for  $i = 0.1$  and 0.26, a plateau value of less than 1.0 was obtained for the case of  $i = 1.0$ . A plateau value of 1.0 is expected for a 1:1 association of TTAB with ionized carboxyl groups. It is proposed that a 1:1 complex of TTAB with PAA may not be possible due to geometric restrictions arising from the size of the tetramethyl head group. This is illustrated in the simple geometric representation of the PAA-TTAB complex given in Figure 3. Such an illustration is not meant to suggest that this is the only configuration of PAA to which TTAB can bind. Rather it is meant to

(23) Turro, N. J.; Arora, K. S. *Polymer* 1986, 27, 783.

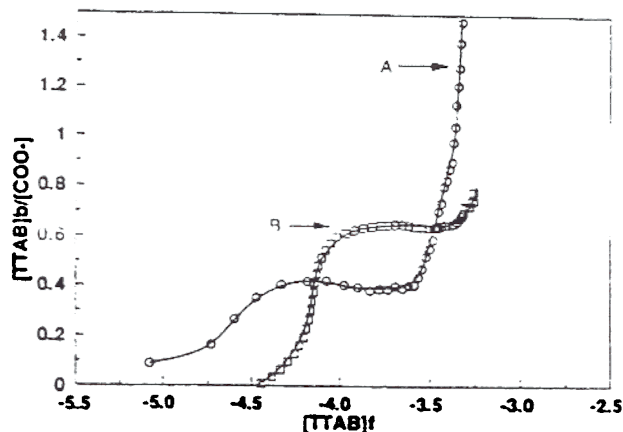


Figure 4. Effect of polymer charge density on TTAB binding to PMA, in 0.01 M NaBr:  $T = 25^\circ\text{C}$ ,  $[\text{PMA}] = 5.0 \times 10^{-4}$  equiv  $\text{L}^{-1}$ ; curve A,  $i = 0.25$ ; curve B,  $i = 1.0$ .

depict the closest packed arrangement of the bound surfactant along the contour of the polymer. In this representation the carboxyl groups are situated on opposite sides of the  $x$ - $y$  plane but on the same side of the  $y$ - $z$  plane as shown in Figure 3. As suggested earlier, the binding of TTAB to PAA is cooperative and indicates interaction between nearby hydrocarbon tails of bound surfactant molecules. Thus it can be imagined that TTAB molecules bind to carboxyl groups alternating above and below the  $x$ - $y$  plane. In this arrangement, the hydrocarbon tails of the bound surfactants could interact across the  $x$ - $y$  plane and with TTAB bound to the next nearest site on the same side of the plane. Now, if we assume that the head group of TTAB is a sphere centered at a carboxyl group, the maximum binding fraction due to packing constraints is given by the ratio of the distance  $L$  to the radius of a TTAB head group. The length  $L$  is calculated to be 2.76 Å from measurements made on CPK<sup>®</sup> space filling models. Thus the maximum binding fraction can be represented as

$$\beta = L/(R_{\text{TTAB}}) \quad (5)$$

where  $R_{\text{TTAB}}$  is the head group radius of TTAB. Analysis of the surface tension data of TTAB in 0.01 M NaBr using the Gibbs equation yielded a value of 3.28 Å for  $R$ . Substitution of this value into eq 3 yields a maximum binding fraction of 0.84. This corresponds well with the observed plateau value of 0.84 for  $\beta$ . The value of the distance  $S$  across the  $x$ - $y$  plane between adjacent carboxyl groups is calculated to be 6.97 Å using a value of 6.40 Å for  $D$  measured from the CPK<sup>®</sup> models. This distance is greater than the diameter of the TTAB head group and thus would not affect the maximum binding fraction. For the case of  $i = 0.10$ , 0.26, and 0.50 the value of  $L$  is on average about 2, 4, and 10 times greater than for  $i = 1.0$  so that the maximum binding fraction could not be considered to be controlled by packing constraints. In this case coiling of the polymer is required to bring ionized carboxyl groups close enough for interaction of bound surfactant molecules to occur.

**PMA-TTAB System.** Binding isotherms of TTAB to PMA were obtained under the same conditions as those for the PAA-TTAB system. However before a comparison of the PMA-TTAB and PAA-TTAB systems is made, several characteristics of the PMA-TTAB system will be discussed.

The binding isotherms of TTAB to PMA for  $i = 0.26$  and  $i = 1.0$  are given in Figure 4. At  $i = 0.26$ , the systems exhibit a slow rise in the initial region followed by a plateau

at a binding fraction around 0.4. At still higher concentrations, a marked increase in the isotherm is observed. Similar two-step binding isotherms have been reported by Shirahama and Tashiro<sup>14</sup> for the 1-decylpyridinium bromide-poly(vinyl sulfate) (PVS) system and by Shimizu et al.<sup>12</sup> for 1-dodecylpyridinium bromide/dodecyltrimethylammonium bromide-hydrophobic alternating copolymers of maleic acid. In the present case, at the plateau, more than 50% of the ionized carboxyl groups are not associated with TTAB. One explanation for this behavior is related to the conformation of PMA at the low pH corresponding to  $i = 0.26$ . It has been shown that for pH values less than 5, PMA adopts a compact coil structure.<sup>15,16</sup> Our work as well as that published elsewhere,<sup>17,18</sup> clearly have shown that these structures have hydrophobic regions which are capable of solubilizing hydrophobic fluorescent probes such as pyrene. On the basis of these observations, it can be suggested that the initial binding occurs either onto hydrophobic sites or onto accessible ionized carboxyl groups. The latter is based on the assumption that some of the carboxyl groups are inaccessible because of the coiled nature of PMA. Above the free surfactant concentration of  $3 \times 10^{-4}$  M, the value of  $\beta$  is seen to increase markedly. The binding isotherm at this point is almost vertical which is indicative of a highly cooperative process such as micellization. It is possible that beyond the plateau, the coiled chain is forced open rendering the hidden carboxyl groups accessible to the surfactant. One possible mechanism for the uncoiling of the polymer is the continued binding of surfactants to accessible sites in the interior of the structure resulting in increased electrical repulsion and the consequent destabilization. Note that the cmc of TTAB in 0.01 M NaBr is  $1.56 \times 10^{-3}$  M, which is higher than the concentration corresponding to the steep rise on the binding isotherm. Also slight turbidity was observed in the solution prior to this rise in the binding isotherm.

Surfactant binding isotherms, similar to the one obtained for the PMA-TTAB system at  $i = 0.26$ , exhibiting a plateau followed by a marked increase in binding, are not uncommon in protein-surfactant systems.<sup>24</sup> In these latter cases, the rise beyond the plateau is considered to be due to the opening up of the protein by surfactant species. It appears that PMA with hydrophobic methyl group also exhibits a compact coiled structure like protein and opens up when surfactant is added to the system. Thus, PMA may be an interesting model for certain types of protein interactions because of its unique structure at low pH values. As mentioned earlier, Shirahama and Tashiro<sup>14</sup> have observed similar binding isotherms for the 1-decylpyridinium bromide (DePBr) to poly(vinyl sulfate) (PVS). In the case of the DePBr-PVS system, a plateau region was obtained at a  $\beta$  of about 0.65. This system is similar to PAA-TTAB at  $i = 1.0$ . They attributed the low plateau value to a decrease in the polymer ionization due to surfactant binding below the critical value predicted by Manning's theory. It is also possible that the low plateau value results from geometric constraints similar to those discussed above for the PAA-TTAB system. Shimizu et al.<sup>12</sup> have attributed the first step to binding to sites where both electrostatic and hydrophobic interactions played a role and the second increase to only electrostatic sites. Interestingly, the first step was steeper than the second in this case.

For PMA at  $i = 1.0$ , the initial binding is similar to that observed for PAA. The plateau value of  $\beta$  for the PMA-

(24) Schwuger, M. J.; Bartnik, F. G. In *Anionic Surfactant-Biochemistry, Toxicology, Dermatology*; Gloxhuber, C., Ed.; J. Wiley and Sons: New York, 1980; Vol 10.

TTAB system at  $i = 1.0$  is much lower than that for the PAA-TTAB system but significantly higher than that for PMA at  $i = 0.26$ . The lower plateau value of  $\beta$  for the PMA-TTAB system at  $i = 1.0$  may be the result of steric hindrance due to the presence of the methyl group on PMA and packing constraints similar to those suggested earlier for PAA at  $i = 1.0$ .

### Conclusions

The effect of charge density on the binding of TTAB to PAA and PMA has been studied using a surfactant-sensitive membrane electrode. The charge density of the polymers was varied by changing the solution pH. Contrary to expectations the onset of surfactant binding at  $i$  values of 0.50 and 1.0 begins at the same free surfactant concentration. This result can be attributed to a combination of two effects, namely, Manning's counterion condensation effects which states that the effective charge density of PAA and PMA will be constant when the degree of polymer ionization is above a critical value,  $i_c$ , and the high NaBr concentration in the system because of which the salt essentially controls the charge density. For PAA and PMA, the critical degree of ionization is 0.38. Below the critical degree of ionization ( $i = 0.10$  and  $0.26$ ), the onset of binding shifts to lower free TTAB concentration compared to those cases above the critical value ( $i = 0.50$  and  $1.0$ ). We have attributed this apparent contradictory

result, below  $i_c$ , to favorable changes in the conformation and hydrophobicity of the polymer and their role in TTAB binding.

The plateau binding fraction for the PAA-TTAB system is less than the expected value of unity for the case when the charge density is 1. This is thought to result from packing constraints due to the TTAB head group size. At lower charge density of 0.10, 0.26, and 0.50, the plateau binding fraction attains unity and even shows marked increase beyond this plateau region.

Finally, PMA at low charge density ( $i = 0.26$ ) shows a slow rising isotherm in the initial part followed by a plateau at about a binding fraction of about 0.4 and sharp increase above about  $3 \times 10^{-4}$  M. This initial slow rise may be due to binding onto hydrophobic sites and the sharp rise to co-operative binding involving electrostatic interactions. It is also possible that the coiled nature of the PMA chain at low charge density renders a significant number of ionized carboxyl groups unavailable initially for surfactant binding but opens up beyond a certain level of surfactant binding. At higher charge density, the PMA chain uncoils, exposing the ionized carboxyl groups, and the observed behavior in this case is similar to PAA at high charge density.

**Acknowledgment.** The authors thank Unilever Research U.S. for financial support of this research.