Study of Surfactant–Polyelectrolyte Interactions. Binding of Dodecyl- and Tetradecyltrimethylammonium Bromide by Some Carboxylic Polyelectrolytes

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ABSTRACT: Binding isotherms are reported for dodecyl- and tetradecyltrimethylammonium (DTA$^+$ and TTA$^+$) ion binding to polyacrylate (PA), alginate, pectate, and (carboxymethyl)cellulose (CMC) in the presence and absence of added NaCl at 30 °C, determined by using a potentiometric technique based on surfactant cation selective solid-state membrane electrodes. The results indicate a highly cooperative nature of the binding process of DTA$^+$ and TTA$^+$ by PA, alginate, and pectate but a lower cooperativity in the CMC system. TTA$^+$ binding results in a larger cooperative binding constant (Ku) in all systems. The differences between DTA$^+$ and TTA$^+$ in the free energy of surfactant binding are $2.19kT$ for PA, $2.50kT$ for alginate, $2.56kT$ for pectate, and $2.64kT$ for CMC without NaCl and $2.42kT$ for PA with 0.01 m NaCl. These differences are comparable to the free energy of transfer of two methylene groups from water to a hydrocarbon medium or to a micelle. The presence of 0.01 m NaCl results in smaller Ku values and higher cooperativity.

Introduction

The binding of ionic surfactants by polyelectrolytes of opposite charge has been reported to be a highly cooperative process. This cooperativity is most often attributed to the contribution of hydrophobic interactions between bound surfactants.[1,3] In previous publications[1,2] we presented the results of an experimental study of the binding of a cationic surfactant, dodecyltrimethylammonium bromide (DTABr), by the anionic polyelectrolytes sodium dextran sulfate (NaDxS) and sodium poly(styrenesulfonate) (NaPSS), in aqueous solution in the presence of added salts such as NaCl, MgCl$_2$, ZnCl$_2$, CaCl$_2$, and LaCl$_3$. Even though the two polymers used have a similar charge density parameter (i.e., average linear charge separation on the polymer backbone), both the binding constant and the degree of cooperativity were found to be widely different for DTA$^+$ binding to DxS or PSS. In the present paper we extend these measurements to a number of synthetic and naturally occurring polyelectrolytes containing carboxylic groups as fixed charges, and we compare the binding of DTA$^+$ and tetradecyltrimethylammonium ions (TTA$^+$). Sodium polyacrylate (NaPA), sodium pectate, sodium alginate, and sodium (carboxymethyl)cellulose (NaCMC) are used. The interaction between cationic surfactants and these polymers will allow us to study the influence of polyion charge density and polyion structure on the binding process. In addition, the interaction between these polymers and surfactants is of importance in systems as diverse as drilling muds and pharmaceutical formulations. Of the polymers studied, PA is more flexible than the ionic polysaccharides except dextran sulfate and is comparable to PSS in hydrophobic and polyelectrolyte character. Pectate (polygalacturonate) behaves as a highly selective ion exchanger in exchange reactions of mono- and divalent cations, while alginate, in which poly(D-mannuronic acid) is the main component, is less selective in cation exchange.[14] CMC is slightly more hydrophobic than pectate and alginate because of the methylcarboxy side group.

Experimental Section

Purified and well-characterized sodium pectate (uronic acid content 90.5%, degree of esterification 1%, 9.5% neutral sac-

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charides, including D-galactose, L-arabinose, D-glucose, D-xylose, and L-ramnose) was kindly supplied by Dr. R. Kohn, Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Czechoslovakia. A sample of sodium (carboxymethyl)cellulose (NaCMC), "Enka HZ900", and sodium alginate, "Kelcosol Algin", were supplied by Enka Industrial Colloids, Arnhem, The Netherlands, and Kelco Co., Clark, NJ, respectively. The samples were dissolved in distilled and deionized water followed by precipitation by ethyl alcohol. The precipitates were washed with a 2:1 ethanol–water mixture until no chloride could be detected in the final rinse solutions.[15] After they were dried under vacuum at 50 °C and dissolved in water, the samples were ion exchanged to the acid form by batch treatment with Dowex 50W-X8 ion exchanger. The sodium level in the resulting solutions was found to be less than 1×10^{-5} mol/L as determined by atomic absorption spectrometry. A small sample of the acid-form solution was used for standardizing and equivalent weight determinations; the remainder was neutralized with NaOH to pH 7. Commercially available poly(acrylic acid) (PA) of molecular weight 250 000 (Aldrich) was used without further purification. The sodium salt (NaPA) was prepared with titration with NaOH. DTABr and TTABr were purchased from Sigma Chemical Co., St. Louis, MO, and purified by repeated recrystallization from acetone. Vacuum-dried reagent grade sodium chloride was used without further purification.

Equilibrium concentrations of free cationic surfactant were determined potentiometrically with a surfactant-selective solid-state electrode that has been reported to have an excellent selectivity for surfactant cations in the presence of even a large excess of simple salt and exhibits Nernstian response over a wide concentration range.[1,2,16,17]

All measurements were carried out at 30 °C at neutral pH without pH buffer.

Results and Discussion

Polyelectrolytes may be characterized by the linear charge density, defined by

$$\xi = e^2/\epsilon bkT \qquad (1)$$

where e is the protonic charge, ϵ the dielectric constant of the solvent, k the Boltzmann constant, T the temperature, and b the average linear charge distance on the polymer. Values of ξ and b for the polymers used in this study are given in Table I. PA is 100% carboxylated. The degree of substitution of the CMC used (Enka HZ900) was determined to be 0.96. Alginate is a linear polysaccharide composed of two types of uronic acids, D-mannuronic acid units linked by diequatorial trans-glycosidic β-(1→4) bonds and L-guluronic acid units linked by diaxial trans-glycosidic α-(1→4) bonds. In alginate, mannuronic and guluronic

Table I
Cooperative Binding Constant Ku and Cooperative Parameter u at 30 °C and the Structural Parameter ξ of Polyelectrolytes

polymer	[NaCl]/ mol kg^{-1}	TTABr		DTABr			
		$10^{-3}Ku/$ mol^{-1} kg	u ($\pm 20\%$)	$10^{-3}Ku/$ mol^{-1} kg	u ($\pm 20\%$)	ξ	b/Å
PA		245	20	26.9	15	2.83[a]	2.52
	0.01	30.5	600	2.69	500		
alginate		29.9	150	2.45	70	1.43	5[b]
	0.01	7.5	2000				
pectate		28.8	60	2.24	70	1.61	4.35[b]
	0.01	7.2	2000				
CMC		25.1	7	1.78	4	1.32	5.35[b,c]
	0.01	6.9	30				
DNA[f]		107	20	9.3	6	4.19[d]	1.70
	0.01	16.6	200	1.38	70		
DxS[g]	0.01			24.0	650	2.80[e]	2.55

[a] Reference 32. [b] Reference 33. [c] 96% substituted. [d] Reference 28. [e] Reference 34. [f] Reference 27. [g] Reference 1.
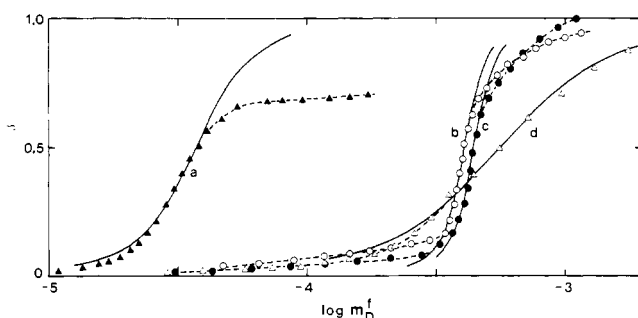

Figure 1. Binding isotherms of DTA$^+$, no added salt, at 30 °C and $m_p = 1.00 \times 10^{-3}$ equiv/(kg-H$_2$O): (a) PA ($m_p = 5.0 \times 10^{-4}$ equiv/(kg-H$_2$O)); (b) alginate; (c) pectate; (d) CMC.

acid units are present in homopolymeric blocks of each of these acid monomers as well as in alternating sequence blocks.[18] Pectate is a linear polymer of D-galacturonic acid, linked by diaxial trans-glycosidic α-(1→4) bonds. With D-mannuronic acid as its main component, the alginate used in the present study may be assumed to have a slightly more extended and flexible structure than pectate, due to the trans-diequatorial β-(1→4) bonds giving alginate a flat, ribbon-like structure where pectate has considerable rigidity due to the diaxial α-(1→4) bonds of its D-galacturonic acid units.[19] In pectate, the advance per glucoside unit is taken as 4.35 Å, although it should be noted that this number is based on X-ray diffraction data on solid calcium pectate.[20-23]

Binding isotherms, plotted as the degree of binding β (β equals the fraction of ionic sites on the polymer occupied by bound surfactants: β = (bound surfactant concentration)/(polyion equivalent concentration)) vs. the free surfactant concentration m_D^f are shown in Figures 1–3, both in the absence and in the presence 0.01 m NaCl. In the absence of NaCl the binding isotherms for PA tend to level off at $\beta = 0.7$, where β values for DTA and TTA binding to the other polymers tend toward $\beta = 1$. Although the charge density parameter ξ is about 20% lower for alginate than for pectate, due to the extended structure of the poly(D-mannuronic acid) segment in alginate,[21] the binding isotherms for both polymers are very similar. Binding to CMC starts at a free surfactant concentration comparable to that for alginate and pectate, but the slope of the β-m_D^f curve is much less for CMC, indicating a lower cooperativity in the binding process.[1,2,7] These observations closely parallel the differences observed between DTA binding to the hydrophobic polyion PSS and the hydrophilic polyion DxS.[1] Adding NaCl (Figure 3) results in a shift of the binding region to higher free surfactant concentrations and also gives steeper binding isotherms, i.e.,
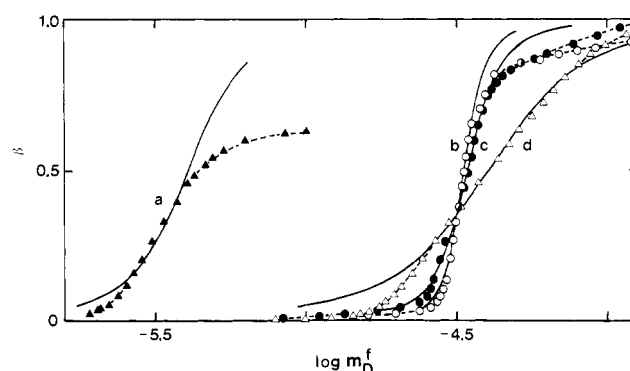

Figure 2. Binding isotherms of TTA$^+$, no added salt, at 30 °C and $m_p = 1.00 \times 10^{-3}$ equiv/(kg-H$_2$O): (a) PA ($m_p = 5.0 \times 10^{-4}$ equiv/(kg-H$_2$O)); (b) alginate; (c) pectate; (d) CMC.
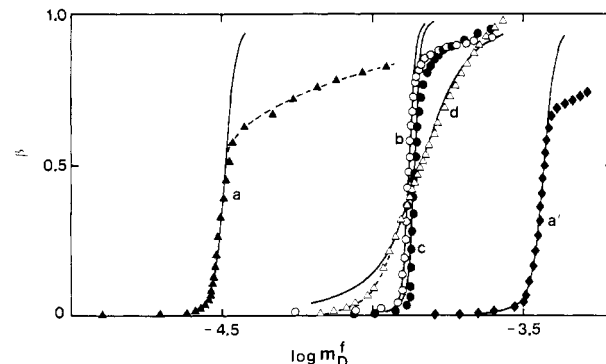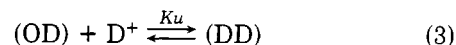

Figure 3. Binding isotherms of TTA$^+$ with 0.01 m NaCl at 30 °C and $m_p = 1.00 \times 10^{-3}$ equiv/(kg-H$_2$O): (a) PA ($m_p = 5.0 \times 10^{-3}$ equiv/(kg-H$_2$O)); (b) alginate; (c) pectate; (d) CMC; (a') PA–DTA$^+$.
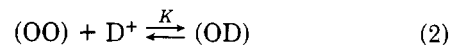
apparently higher cooperativity of the binding process.

Consider the following binding equilibria:

$$(OO) + D^+ \xrightarrow{K} (OD) \tag{2}$$

$$(OD) + D^+ \xrightarrow{Ku} (DD) \tag{3}$$

where O represents a binding site on the polymer, D$^+$ the surfactant ion, and D an occupied site on the polymer. Thus OO represents two neighboring unoccupied sites, and DD two neighboring occupied sites. The binding constant Ku describes the binding of surfactant to a site adjacent to a site already occupied by surfactant. The corresponding free energy change is given by $kT \ln Ku$, equivalent to the free energy of transfer of surfactant ions from the bulk solution to the polymer–surfactant complex environment. The parameter u, which is called the co-

operativity parameter, is defined as

$$u = (DD)(OO)/(DO)^2 \qquad (4)$$

where the parentheses denote concentration units. Thus (OD) stands for the concentration of isolated bound surfactants. Equation 4 indicates that u is the equilibrium constant for the aggregation process of surfactants bound to the polymer. Applying the Zimm–Bragg theory for the helix–coil transition of biopolymers[24] to the cooperative binding process described above, Schwarz,[25] and later Satake and Yang,[7] derived the following expressions:

$$\beta = 1/2\{1 + (s - 1)/[(1 - s)^2 + 4s/u]^{1/2}\} \qquad (5)$$

$$(m_D^f)_{0.5} = (Ku)^{-1} \qquad (6)$$

$$(d\beta/d \ln m_D^f)_{0.5} = u^{1/2}/4 \qquad (7)$$

where s equals Kum_D^f and $(m_D^f)_{0.5}$ is the concentration of free surfactant at the half-bound point ($\beta = 0.5$). Although the nearest-neighbor model described in eq 2 and 3 is an obvious oversimplification given the complex phenomena considered here, phenomena that may include polymer conformation changes and the formation of large hydrophobic regions, the Satake–Yang treatment serves as a convenient formalism to consider the influence of surfactant-surfactant interactions on the binding process.

By using K and u as adjustable parameters, one can compare the observed binding isotherms to the predictions from eq 5–7. Best values of Ku and u for the cases reported here are given in Table I. The binding isotherms as calculated from eq 5, using the Ku and u values given in Table I, are represented by the solid lines in Figures 1–3.

The observed order for Ku is PA $\gg$ alginate $\geq$ pectate $>$ CMC, where the order for ξ is PA $\gg$ pectate $>$ alginate $>$ CMC. The ξ value for alginate is calculated by using $b = 5$ Å for poly(mannuronic acid), based on X-ray diffraction data for a solid- or gel-phase sample. We may speculate that for the more flexible alginate (polymannuronate) polymer, the charge-to-charge distance in solution is slightly less than the 5-Å spacing observed in the ordered solid or gel phase.[20,22] Alginate also contains a poly(guluronic acid) segment of $b = 4.36$ Å, equivalent to a ξ value of 1.61.[23] Alginates from commercial brown algae, except *Laminaria hyperborea*, contain about 40% guluronic acid and 60% mannuronic acid; the polymer is made up of about 20% poly(guluronic acid) segments, 40% poly-(mannuronic acid) segments, and 40% alternating segments.[18,26] The presence of the guluronic acid segments may again result in lower b values, estimated at 4.87–4.74 Å (ξ value between 1.48 and 1.52) on the average. Thus the charge density parameter of alginate, due to its greater flexibility and to the guluronic acid segments, may be closer to the pectate value than is indicated in Table I. Generally, the values of Ku seem to follow the order in ξ in these carboxylated polyelectrolytes, but no correlation between Ku and ξ is found when the previous data for dextran sulfate (DxS)[1] and DNA,[27] also shown in Table I, are taken into account. For instance, the value of Ku for the DTA+–DxS system in the presence of 0.01 m NaCl is much larger than Ku for the corresponding DTA+–PA system, even though ξ is similar for both polyelectrolytes. On the other hand, Ku for the DNA systems is smaller than Ku for the PA systems, though ξ for DNA is much larger than ξ for PA.

Since the cooperative effect in the binding of surfactant by linear polymers is considered to be caused by the hydrophobic interaction between bound surfactants, we may expect this effect to be sensitive to the neighboring charge-to-charge distance on the polymer. Thus a small cooperative parameter for the CMC system might be ex-

pected because of the longer average separation between neighboring ionic sites. Although b values for pectate and alginate are only slightly smaller than the corresponding value for CMC, the cooperativity parameter u is very much higher for the pectate and alginate systems, even higher in fact than u for the PA system, a polymer with a much smaller linear charge separation ($b = 2.52$ Å). It seems obvious from these observations that the detailed structural properties of the polymer play an important role in the surfactant binding process. Although the charge density of the polymer is an important parameter, other factors such as hydrophobic character, flexibility, and detailed local structure of the polymer also strongly influence both the binding constant Ku and the cooperativity parameter u.

We now consider the observed differences between DTA+ and TTA+ binding. From the values of u for DTA+ and TTA+, the difference in the corresponding free energy change of the aggregation process of DTA+ and TTA+ can be estimated to be $0.3kT$ for PA, $0.8kT$ for alginate, $-0.2kT$ for pectate, and $0.6kT$ for CMC in the case of salt-free systems and $0.2kT$ for PA with 0.01 m NaCl. Because of the high uncertainty in u, each of these numbers is approximately $\pm 0.2kT$. The corresponding values are $1.1kT$ with 0.01 m NaCl and $1.2kT$ without salt for DNA.[27] This observation indicates that in the case of the carboxylic polyelectrolytes studied here the contribution of the surfactant chain length to the cooperativity of the binding process is much smaller than is the case for DNA. Both for DTA+ and for TTA+ binding to PA, the values of Ku in the 0.01 m NaCl added system are about one order of magnitude lower than in the salt-free system. However, for pectate, alginate, and CMC, the difference in Ku between the 0.01 m NaCl added system and the salt-free system is much smaller. It should be noted that the polymer concentration used in the PA systems (5×10^{-4} equiv of carboxylate/kg of H$_2$O) is half that of the concentration in the salt-free polysaccharide systems, and thus the concentration of competing Na+ counterions is proportionally lower in the PA systems. The slopes of the plots of log (Ku) vs. log (total Na+ concentration) are -0.67 for TTA+–PA, -0.58 for TTA+–alginate, -0.58 for TTA+–pectate, -0.54 for TTA+–CMC, and -0.75 for DTA+–PA. These slopes are comparable to the dependence of Ku on added NaCl concentration for the DTA+–DxS system.[1] According to the simple condensation model of polyelectrolyte solutions, a constant fraction of the counterions is trapped in the close vicinity of the polymer backbone, reducing the polyions' effective charge density parameter to $1/z$, where z is the counterion charge (i.e., $+1$).[28] Thus the binding of surfactant counterion would not influence the effective linear charge density parameter of the polyion until ξ_{net} reaches a value of unity (for monovalent counterions). From this consideration, a slope of -1 in the plot of log (Ku) vs. log [Na+] would be expected. The lower slopes observed above suggest an incomplete exchange reaction between surfactant and Na+. The slopes given above are equivalent to a 1:0.6 exchange reaction with a Na+ counterion.[29] This implies that the linear charge density parameter is not constant during the surfactant binding process.

Finally, we observe that from the difference in Ku between DTA+ and TTA+, we calculate the difference in the free energy of surfactant binding between DTA+ and TTA+ as given by the KT ln (Ku) term to be $2.19kT$ for PA, $2.50kT$ for alginate, $2.56kT$ for pectate, and $2.64kT$ for CMC in the case of the salt-free systems and $2.42kT$ for PA with 0.01 m NaCl. These values (($1.10-1.32)kT$ per

methylene group) are comparable to the free energy of transfer of a methylene group ($(1.08-1.32)kT$) from water to hydrocarbon or micelle.[8,32] This observation points out the similarity between the binding of surfactant by polyelectrolyte and micelle formation, presumably because both processes involve a transfer of ionic surfactant from water to a highly charged and hydrophobic colloidal particle environment of surfactant–polyelectrolyte complex or micelle.[31]

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Secondary Transitions in Amorphous Polymers. 5. Linear Form of the Tait Equation Applied to Isotactic Poly(methyl methacrylate)

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ABSTRACT: An exact linear form of the Tait equation is used to analyze isothermal specific volume–pressure data on isotactic poly(methyl methacrylate) above its glass transition temperature. Since linear Tait behavior is obviously not obeyed in regions containing pressure-induced transitions, other polynomial and multisegment correlations are examined, with the standard error taken as the main criterion of model performance. An automatic computer technique has been developed to systematically test multisegment correlations of $y = f(P)$ data to locate intersection pressures, P^i, along individual isotherms. A three-segment correlation gives the best results on four high-temperature isotherms (138.2, 160.7, 174.5, and 190.2 °C), indicating the existence of secondary relaxations in the pressure range 1–2000 bars. These results are strengthened by good correlations of the determined transition points in a T–P plot, both among themselves and in comparison with prior results. Unambiguous interpretation of two lower isotherms (90.4 and 116.3 °C) is more difficult because of experimental uncertainties and the existence of the glass transition in the high-pressure region. Secondary relaxations above T_g include two liquid–liquid transitions, the intermolecular (T_{ll}) and the intramolecular ($T_{ll'}$), and a low-pressure glass transition, $T_g(\mathrm{LP})$. Evidence for T_β elevated above T_g at high pressure is also found. Pressure coefficients for these transitions are given.

Introduction

The Tait equation has been used extensively in recent years to represent volume–pressure isotherms on polymers[1-13] and low molecular weight liquids.[14,15] In its integrated form, it is usually quoted as

$$1 - V/V_0 = C' \ln (1 + P/b) \qquad (1)$$

where V is the specific volume in cm³/g at pressure P, and V_0 is the corresponding volume at the reference pressure

$P = 0$ bar. (Some authors use a reference pressure of $P_0 = 1$ bar,[14] but more generally, it is given as $P_0 = 0$ bar, even in cases where the tabulated data begin at $P = 1$ bar.[9]) C' is taken as a universal constant, having a value of 0.0894, as defined by Simha et al.[5-10] The parameter b is a constant along any isotherm for which there is no pressure-induced transition. In the presence of such a transition, the data points deviate from eq 1, and b effectively increases. The initial value of b between P_0 and the first