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Electrokinetics of Muscovite Mica in the Presence of Adsorbed Cationic Surfactants

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Received December 19, 1990. In Final Form: June 25, 1991

The electrokinetic properties of muscovite mica in the presence of four hexadecylammonium (CTA) salts and two dihexadecyldimethylammonium (DHDA) salts have been studied using a flat plate streaming potential technique. The potential results obtained for dihexadecyldimethylammonium acetate (DHDA) and bromide (DHDAB) systems are compared with literature values obtained from the direct force balance technique. Good correlation between the two techniques is observed for the DHDAB system. For the DHDA system, an analysis of the streaming potential results using a triple-layer model for the substrate-aqueous solution interface yields a degree of dissociation of the DHDA molecule of $\approx 20\%$. This is considerably lower than the value of $\approx 100\%$ obtained from the direct force balance technique. Possible reasons for the differences between the results of the two techniques are discussed. The potential results obtained for the CTA salts studied were used to obtain an order in the degree of counterion binding, which was 3,5-dichlorobenzoate > 3,4-dichlorobenzoate > 4-chlorobenzoate $\approx \text{Cl}^-$. This order agrees with solution conductivity results.

Introduction

A significant body of work exists on the adsorption of ionic surfactants at solid-aqueous solution interfaces. The understanding of the structure of such surfactants at solid-aqueous solution interfaces comes almost exclusively from detailed adsorption isotherms plus supporting electrokinetic studies on high specific surface area aqueous colloids.

Recent advances have come from direct force measurements between mica surfaces¹ with adsorbed or Langmuir-Blodgett deposited monolayer or bilayer surfactant films. The direct force measurement data reveal subtle structural, hydrophobic, and hydration force effects as mediated by surfactant layer structure and thickness and by counterion association. The role or effect of electrostatic interactions between two mica surfaces with adsorbed surfactant is extracted from force-distance data by using the electrostatic interaction energy and hence the surface potential as an adjustable parameter.

We seek to support such force-distance data with the direct measurement of the electrostatic or ζ potential of mica with adsorbed monolayers and bilayers of ionic surfactants. We have therefore focused on systems for which force-distance data are currently available and/or to which directly measured electrokinetic potential data are required or thought relevant to assist the deconvolution of direct force measurements.

Double and single alkyl chain quaternary ammonium surfactant salts that are known to adsorb as a bilayer to mica were chosen for study. The double-chain surfactants were dihexadecyldimethylammonium (DHDA) salts. These surfactant salts are soluble with anionic counterions such as acetate and hydroxide but quite insoluble with bromide and chloride.² This behavior is related intimately to the degree of counterion binding to the ammonium head

group and results in the formation of spontaneous aggregates in bulk solution for the soluble species at amphiphile concentrations as low as $1 \times 10^{-5} \text{ mol dm}^{-3}$. Video-enhanced differential interference contrast microscopy (VEDICM) shows these aggregates to be single bilayer plates at amphiphile concentrations of 1×10^{-4} to $1 \times 10^{-3} \text{ mol dm}^{-3}$ (20°C) that form vesicles or possibly micelles at temperatures above the DHDA chain melting temperature of $\approx 40^\circ\text{C}$.³ At 20°C , with an acetate counterion, and at a DHDA concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$, a bilayer adsorbs to the basal plane of mica.^{3,4} Shorter chain homologues such as didodecyldimethylammonium salts show a micellar phase at higher concentrations that finally collapses to a lamellar structure at $\approx 1.0 \text{ mol dm}^{-3}$.⁵⁻⁸

The hexadecyltrimethylammonium (CTA) salts were chosen to investigate the electrokinetics of a single alkyl chain quaternary ammonium surfactant adsorbed as a bilayer onto mica. These salts are available with a number of counterions and examples having the chloride, the 3,4-dichlorobenzoate (3,4-Cl), the 3,5-dichlorobenzoate (3,5-Cl) or the 4-chlorobenzoate (4-Cl) counterions were investigated. These surfactant salts show a wide range of counterion binding and critical micelle concentration (cmc) behavior.⁹ Although direct force measurements using this range of counterions are not complete, a comparison of electrokinetic data with the bromide counterion will assist in understanding the direct force measurements on such salts at the mica-water interface.

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Table I. cmc's and Degree of Counterion Dissociation (α) Information for CTA Salts in Aqueous Solution

species	cmc _I , ^a mM	cmc _{II} , ^b mM	α_I ^a	α_{II} ^b	temp, °C	ref
chloride	1.300				30	13
4-Cl	0.196	0.312	0.43	0.18	29	12
3,4-Cl	0.134		0.15		29	12
3,5-Cl	0.104		0.10		29	12

^a Primary cmc. ^b Secondary cmc denoted by a phase transition.

Experimental Section

Electrokinetic measurements were made using a flat plate streaming potential apparatus that has been fully described elsewhere.¹⁰ Briefly, a rectangular cross-section capillary was formed between two mica sheets separated by a Teflon spacer gasket. Streaming potentials were recorded for flow in both directions and a ζ potential calculated using the Smoluchowski relationship.¹¹

$$\zeta = (\eta\lambda/D\epsilon_0)(\Delta E/\Delta P) \quad (1)$$

In this expression, λ is the conductivity of the capillary, D the dielectric constant of the medium, ϵ_0 the vacuum permittivity, η the bulk viscosity, ΔP the pressure drop across the capillary, and ΔE the streaming potential. The measurements were adjusted for the effects of capillary surface conduction.¹⁰ Streaming potential plates were of borosilicate glass and had dimensions $7.5 \times 2.5 \times 0.1$ cm. Mica sheets were glued to these plates with a low melting point ($\approx 80^\circ\text{C}$) inert wax (Shell-Epikote Resin 1002). A small amount of wax was placed on a glass slide and the slide heated to $\approx 100^\circ\text{C}$. A piece of mica was then placed on the slide and pressed firmly. Cooling produced a firm bond that is chemically inert in aqueous systems.¹ The mica was then trimmed to the exact dimensions of the glass slide and cleaved to produce a fresh surface for use in streaming potential measurements. A fresh cleavage surface was prepared for each experiment.

Water used in this study was purified by distillation followed by percolation through charcoal and mixed-bed ion-exchange resins (Millipore, Milli-Q). The final conductivity of the water was less than $1 \times 10^{-6} \text{ S cm}^{-1}$ at 20°C . Sheets of mica were from Bahir, India, and were kindly supplied by Dr. R. Pashley, Australian National University, Canberra. Experiments were performed at $20 \pm 1^\circ\text{C}$ for the DHDA surfactant salts and at $28 \pm 1^\circ\text{C}$ for the CTA surfactant salts. Electrolytes were analytical grade reagents. Electrodes were replatinized if the coating deteriorated or if the asymmetry potential in streaming potential measurements increased to a significant level.

Dihexadecyldimethylammonium acetate (DHDA) was converted from the bromide salt by an ion-exchange technique described by Brady et al.⁶ Purified samples were kindly supplied by Dr. R. Pashley. Analysis showed insignificant levels of chloride salts, the expected contaminant of the ion-exchange process. Solutions were clear at room temperature, indicating the absence of carbonates. Hexadecyltrimethylammonium chloride (CTAC) was from Tokyo Kasei and was recrystallized from acetone. Hexadecyltrimethylammonium salts with the 3,4-dichlorobenzoate, 3,5-dichlorobenzoate, and 4-chlorobenzoate counterions were prepared by metathesis of CTAB plus silver chlorobenzoates as previously described.¹² Cmc and dissociation data for these species are shown in Table I.

The cmc's were determined by a conductivity method, and the degree of dissociation (α) was determined from the ratio of the slope of the conductivity versus concentration plot above

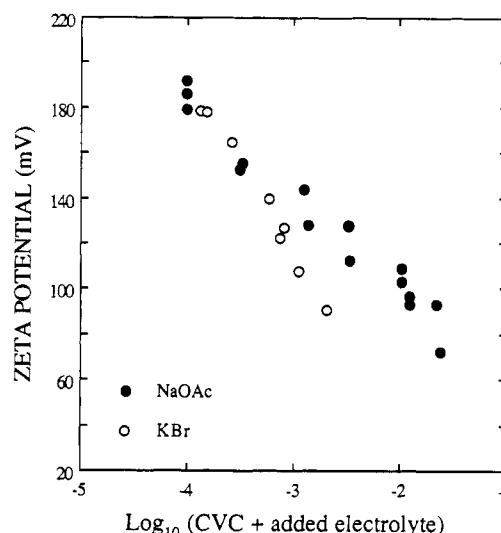


Figure 1. ζ potential of a dihexadecyldimethylammonium acetate bilayer adsorbed to muscovite mica in aqueous solution as a function of the addition of sodium acetate and potassium bromide.

and below the cmc.¹³ This technique is only approximate and gives lower α values than, for example, a pH indicator technique.^{14,15} It does however give a good overview of the relative binding strengths of the various counterions.

Results and Discussion

1. Double-Chain Surfactant Bilayers. The ζ potential of mica in the presence of a solution of $5 \times 10^{-4} \text{ mol dm}^{-3}$ DHDA with additions of sodium acetate at concentrations from 0 to $3 \times 10^{-2} \text{ mol dm}^{-3}$ is shown in Figure 1. The ζ potentials were corrected for the effects of surface conduction at total electrolyte concentrations less than $1 \times 10^{-3} \text{ mol dm}^{-3}$ and for the bulk solution viscosity relative to water across the entire concentration range. The horizontal scale is plotted as the logarithm of the critical vesicle concentration (cvc) of the DHDA salt plus the concentration of added sodium acetate. Charged self-assembled aggregates and their dissociated counterions no doubt contribute to the magnitude of the total ionic strength^{3,16} of the system, but since this has not yet been adequately quantified, their contribution has not been included. The cvc for the DHDA molecule was chosen as $1 \times 10^{-4} \text{ mol dm}^{-3}$. This value was deduced from the calculated Debye length (κ^{-1}) for a $5 \times 10^{-4} \text{ mol dm}^{-3}$ solution as calculated by Pashley et al.³ As is to be expected from counterion binding studies,¹⁷ it is considerably higher than the value calculated for dihexadecyldimethylammonium bromide (DHDAB).¹⁸

The ζ potential of mica in the presence of a solution of $5 \times 10^{-4} \text{ mol dm}^{-3}$ DHDA with additions of potassium bromide at concentrations from 0 to $5 \times 10^{-3} \text{ mol dm}^{-3}$ is also shown in Figure 1. The effect of the bromide salt on double-layer electrokinetics is not evident until an addition of approximately $6 \times 10^{-4} \text{ mol dm}^{-3}$ KBr. This is in line with the observations of Pashley et al.³ for the same system. The potentials calculated by these workers for the addition of the KBr electrolyte to DHDA show good correlation

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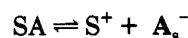
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with the ζ potentials. The addition of KBr at concentrations in excess of $5 \times 10^{-3} \text{ mol dm}^{-3}$ caused aggregation of the surfactants in bulk solution.

To aid in the understanding of the observed ζ potential behavior, the surface was modeled using a site-dissociation model. The model is most easily demonstrated using the data for the addition of KBr to a solution of DHDAAs since the Br^- counterion is known to have a high affinity for the surfactant.

The generalized dissociation equilibrium for the surface-adsorbed species is



where S^+ represents a positive quaternary ammonium surfactant and A_s^- an anion at the surface. The dissociation constant (K_d) for the equilibrium is then

$$K_d = \frac{[\text{S}^+]a(\text{A}_s^-)}{[\text{SA}]} \\ = \frac{([\text{S}^+]a(\text{A}_b^-)/[\text{SA}]) \exp(e\psi_o/kT)}{(2)}$$

where a represents the activity of an anionic species and the b subscript a bulk species. The activities of the surface and the bulk species were equated by assuming a Boltzmann distribution of ions.

The surface charge per unit area (σ_o) is then given by

$$\sigma_o = e[\text{S}^+] \quad (3)$$

where e is the electronic charge, and the total number of surface sites per unit area (N_s) is given by

$$N_s = [\text{S}^+] + [\text{SA}] \quad (4)$$

The electroneutrality condition is then invoked such that

$$\sigma_o + \sigma_d = 0 \quad (5)$$

where σ_d is the diffuse layer charge per unit area. The degree of dissociation for the system (α) is then given by

$$\alpha = [\text{S}^+]/N_s \quad (6)$$

and by solving for $[\text{S}^+]$, one obtains an expression of the form

$$[\text{S}^+] = N_s \left(1 + \frac{a(\text{A}_b^-) \exp(e\psi_o/kT)}{K_d} \right)^{-1} \quad (7)$$

The surface (ψ_o), the inner Helmholtz plane (IHP; ψ_β), and the outer Helmholtz plane (OHP; ψ_d) potentials were then related by assuming a Gouy-Chapman-Stern-Grahame (GCSG) type approach such that

$$\psi_o - \psi_\beta = \sigma_o/C_1 \quad (8)$$

and

$$\psi_\beta - \psi_d = \sigma_d/C_2 \quad (9)$$

where C_1 and C_2 are the capacitances of the inner and outer Helmholtz layers, respectively. This provides an equation system linking all the variables with the input parameters, namely, K_d , C_1 , and C_2 .

Choosing values for C_1 , C_2 , and N_s is not as difficult as for many oxide systems. Numerous studies have shown the position of the shear plane in highly bound surfactant systems to be in close proximity to the plane of the surfactant head groups.^{15,19-22} This allows the choice of C_1 and C_2 parameters close to ∞ . The value of N_s is gleaned

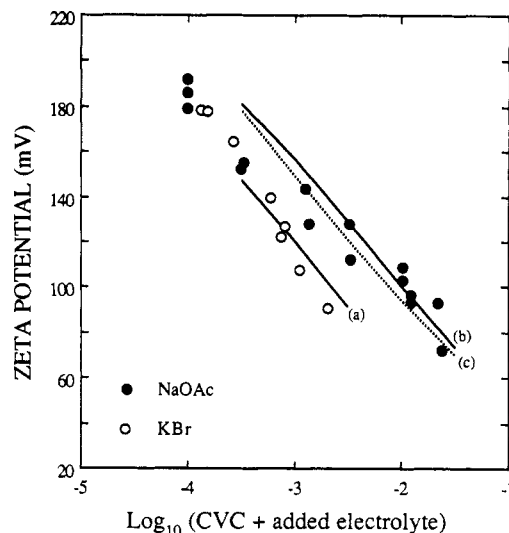


Figure 2. Calculated fits to the data of Figure 1 assuming $N_s = 1.67 \times 10^{14} \text{ sites cm}^{-2}$ and (a) $\text{p}K_d = 2$, $C_1 = C_2 = \infty$; (b) $\text{p}K_d = 1$, $C_1 = C_2 = \infty$; (c) invoking the viscoelectric theory of Lyklema and Overbeek and assuming a field constant of $4 \times 10^{-16} \text{ V}^{-2} \text{ m}^{-1}$.

from volume calculations²³ which show the equilibrium head group area per surfactant molecule to be $\approx 60 \text{ \AA}^2$.

An input value for $\text{p}K_d$ of 1.0 provides a reasonable fit to the ζ potential data for the addition of acetate ions and a $\text{p}K_d$ value of 2 for the addition of bromide ions. The fitted data are shown in Figure 2. The $\text{p}K_d$ value required to fit the bromide ion data is in close correlation with that calculated by Pashley et al.,⁴ namely, 1.88–1.95. However, the $\text{p}K_d$ value for DHDAAs shows poor correlation with the highly dissociated nature of the acetate system predicted from both solution behavior and force balance measurements.

There are a number of possibilities for these anomalies. The first is that for a fully dissociated surface, the infinite value of C_2 chosen for the outer layer capacitance is an overestimation for the undissociated counterion case. This is a reasonable postulate where the counterion is no longer in close association with the surfactant head group. A lower outer plane capacitance results in the predicted ζ potential reaching a maximum as the surface charge increases. For example, at a C_2 value of $200 \mu\text{F cm}^{-2}$, the simple model predicts the same ζ potential (at constant electrolyte concentration) for all surface charges of $\geq 9.0 \mu\text{C cm}^{-2}$, ($\alpha \geq 0.30$). Therefore, to differentiate between differently charged surfaces by an electrokinetic technique, under such circumstances, is theoretically not possible. The difference between experiment and theoretical predictions may simply be that the technique is insensitive to the surface charge.

Another explanation lies in the viscoelectric effect put forward by Lyklema and Overbeek.²⁴ Hunter²⁵ quotes "If one can find a system in which ζ is expected to increase but the observed ζ is found to reach a limiting value, this should provide a means of estimating an upper limit for f ," where f is the viscoelectric field constant. A bilayer of DHDAAs adsorbed to mica is potentially such a system.

With the approximate formula of Lyklema and Overbeek,²⁴ the experimental ζ potential behavior is predicted if a value for f of $4 \times 10^{-16} \text{ V}^{-2} \text{ m}^{-1}$ is used. The fit to the data is also shown in Figure 2. This value for the visco-

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electric constant is similar to the value used to give agreement between force balance and electrokinetic data for 1:1 electrolyte ion interaction with mica.²⁶ In terms of extant theories, the value is not unreasonable. Nonetheless, many workers^{20,27} have calculated values of f of far lower magnitude.

The third possible explanation is that the calculated pK_d value is indeed typical of acetate ion binding to a quaternary ammonium surfactant head group at the solid-solution interface. The data of Bartet et al.¹⁷ for counterion binding to the hexadecyltrimethylammonium surfactant head group give a 10:1 ratio between the dissociation constants of the bromide and acetate ions. This is in line with the values used in this study and is equivalent to an acetate counterion system that is ≈ 15 –20% dissociated. Recent work by Tsao and Evans²⁸ supports the calculated pK_d of 1 used to fit the data in Figure 2. They have made new direct force measurements of DHDA adsorbed on mica as a function of temperature and have reevaluated earlier results³ allowing for hydration forces. Their results show that at 25 °C and at DHDA concentrations less than 10^{-2} M, the degree of dissociation is $\approx 20\%$. This value is in excellent accord with the pK_d value used in Figure 2.

2. Single-Chain Surfactant Bilayers. It was decided to use the CTAC surfactant salt in preference to the bromide form since the former species shows simpler solution behavior as a function of both amphiphile and added electrolyte concentration.²⁹ The mono- and dichlorobenzene CTA salts were studied along with CTAC to elucidate a range of binding effects. These surfactant species show significant viscoelasticity³⁰ and a Krafft temperature of >23 °C. These phenomena were addressed by measuring viscosities for all solutions and by using a solution temperature of 28 °C.

It is known that the hexadecyltrimethylammonium bromide (CTAB) molecule adsorbs to the muscovite mica interface to give a bilayer of adsorbed molecules at or about the cmc. From this and Langmuir-Blodgett deposition data on single alkyl chain molecules,³¹ it was concluded that, for the CTAB molecule, adsorption at ≈ 45 Å² per head group would produce charge neutralization of the underlying mica surface at a pH of ≥ 5.2 . A pH of ≈ 5.9 was calculated in order to produce similar results using the chloride counterion since it is known that it shows lower levels of counterion binding than the bromide salt¹⁷ and thus produces more effective background surface neutralization.

The ζ potentials of 1×10^{-3} mol dm⁻³ solutions of the various CTA surfactant salts adsorbed to mica for sodium chloride additions from 0 to 1×10^{-1} mol dm⁻³ are shown in Figure 3. The potentials were corrected for the effects of surface conduction and for the enhanced viscosity observed in these systems. A typical example of the viscosity as a function of added sodium chloride is shown in Figure 4. As with the double alkyl chain surfactants, the horizontal axis is plotted as the logarithm of the cmc of the CTA salt plus the concentration of added electrolyte. The effect of the charged self-assembly species on the Debye length, if any, was ignored. The effect of added salt on the cmc of the species in solution was also not

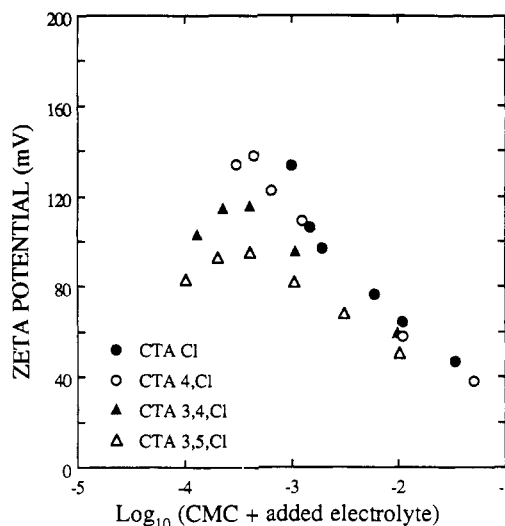


Figure 3. ζ potential of various hexadecyltrimethylammonium salts as a function of the addition of NaCl. The surfactant salts were adsorbed as a bilayer to muscovite mica at pH 5.9 ± 0.2 .

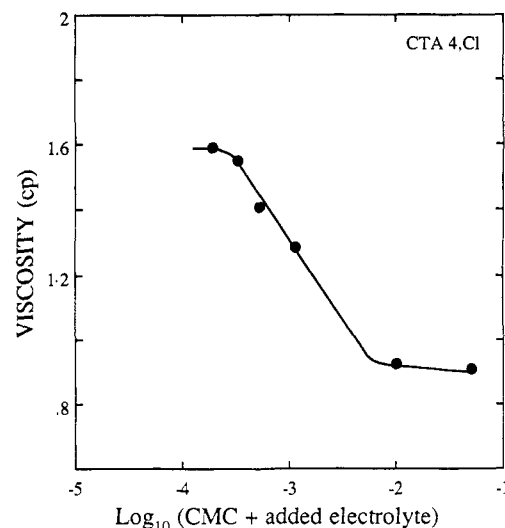


Figure 4. Viscosity of hexadecyltrimethylammonium 4-chlorobenzoate solution as a function of the addition of NaCl at 28 °C.

considered. It would be interesting to consider both of these points in the light of recent analysis of the slope of surface potential data as a function of added salt as measured using potential-sensitive spectroscopic probe molecules.³²

When the ζ potential data for the CTAC species as a function of added sodium chloride are examined, an almost linear relationship is observed, particularly at higher electrolyte additions. The slope of the potential as a function of added salt concentration is 41 ± 2 mV in this concentration regime. A linear relationship between potential and concentration was also observed by Drummond et al.³³ for dodecyltrimethylammonium (DTA) halide micelles where the potential was measured by a spectroscopic probe technique. A slope of ≈ 35 and ≈ 39 mV per 10-fold increase in concentration was observed for the chloride and bromide counterions, respectively. Using a cell model and the assumption of spherical micellar geometry, they calculated the average degree of dissoci-

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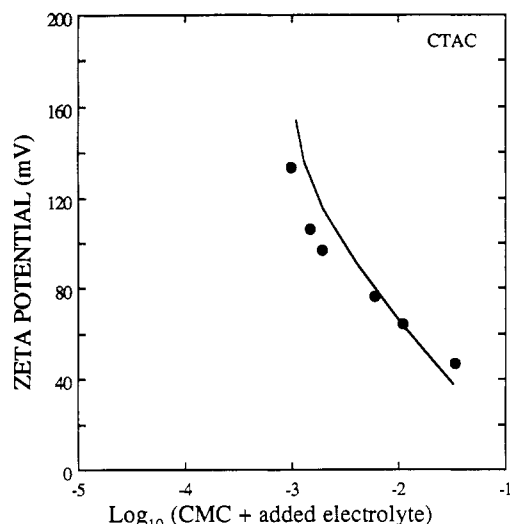


Figure 5. Calculated fit to the ζ potential of hexadecyltrimethylammonium chloride as a function of the addition of NaCl. Fitting parameters are given in the text.

ation (α) as 0.64 and 0.43 for the same two systems. Their value of α of dodecyltrimethylammonium bromide (DTAB) is substantially higher than that calculated using a planar model of the interface for DHDAB.

At lower electrolyte additions, where the total ionic strength approaches the cmc of the CTAC molecule, the analysis of the data is clouded. The inability to quantify the contribution to the total ionic strength of the charged micelles and unbound counterion means the data are more difficult to interpret.

To examine the predictions of the site binding model for the CTAC system, a dissociation constant, K_d , was defined as for the double alkyl chain surfactant molecules. The parameter N_s was chosen as 2.2×10^{14} sites cm^{-2} in line with volume calculations.³⁴ This value is higher than the area per head group data calculated for spherical micelle systems³³ but is reasonable considering we are dealing with a planar surface as distinct from the highly curved interfacial geometry of a micelle. C_1 was given a value of ∞ , assuming close association of the plane of the surfactant head groups and the bound counterions, and C_2 was given a value of $200 \mu\text{F cm}^{-2}$ based on the earlier discussion where a value of ∞ was considered inappropriate for systems that were not fully bound. It should be noted at this point, in modeling terms, the effect of changing C_2 from ∞ to $200 \mu\text{F cm}^{-2}$ on the degree of dissociation is minimal.

A reasonable fit to the CTAC electrokinetic data was obtained with a $\text{p}K_d$ value of 2.0, which represents an $\alpha \approx 0.06 \pm 0.02$ in the electrolyte concentration range of interest. The fit to the data is shown in Figure 5. Two points from this theoretical analysis are noteworthy: (i) The degree of dissociation for the CTAC molecule adsorbed to mica is substantially less than that calculated from micellar studies³³ and less than the double alkyl chain equivalent. (ii) As the concentration of added electrolyte approaches zero, the calculated potential increases rapidly (as does the apparent α).

If one considers counterion binding in these systems, there exists the possibility that the higher head group densities associated with planar relative to curved interfaces is taken up by extra counterion binding. In effect,

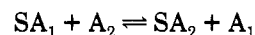
the a parameter in the v/a curvature criteria^{35,36} is adjusting itself by ion binding, thus accommodating the planar bilayer structure. In this description, v is the volume of the hydrocarbon residue, a is the effective head group area, and l is the molecular length of the surfactant. Another possibility is that a full bilayer has not formed since the total concentration of surfactant is of the same order of magnitude as the cmc in solution. Generally, however, a bilayer is found on a solid substrate when the solution concentration of the surfactant is around the cmc.^{37,38}

The last possibility is that the first surfactant layer has not completely neutralized the underlying surface, producing a net negative charge to be compensated. This point is difficult to quantify, but even so, the effect is not large. Calculation of the diffuse layer charge of the mica from Gouy-Chapman theory at a ΔpH of 1 unit from the adsorption pH and addition of this quantity to the measured diffuse layer charge would alter the calculated degree of dissociation by ≤ 0.2 . Therefore, the most likely explanation is that these planar systems show greater counterion binding than in the solution curved interface state.

If one considers the sharp rise in potential as added electrolyte concentration decreases, the effect is almost certainly due to the neglect of the effect of charged surfactant phases and unbound counterions in the calculation of the total ionic strength. To quantify this effect in the absence of extant theories is not worthwhile since incorporation of an empirical explanation in the modeling exercise would produce an uncertainty comparable to the effect. However, it is worth noting that the values of ζ calculated by the simple model should reach an upper limit as the added electrolyte concentration approaches zero.

The data of Figure 3 for the addition of sodium chloride to 1×10^{-3} mol dm^{-3} solutions of mono- and dichlorobenzoate salts of CTA can now be examined in light of the simple theoretical description of the CTAC data. At the limit of zero added electrolyte, the dissociation follows the series $\text{Cl}^- \approx 4\text{-Cl} > 3,4\text{-Cl} > 3,5\text{-Cl}$. This is the same series for the level of counterion binding observed from conductivity data.

The maxima in potential observed in Figure 3 as a function of electrolyte addition at first glance appear counterintuitive. Examined in the light of the expected binding constants for each ion, the maxima are easily described in terms of the equilibria, viz.



where A_1 represents a mono- or dichlorobenzoate ion and A_2 a chloride ion. The evaluation of this equilibrium is once again hampered by an inadequate description of the concentration of A_1 . An approximate description could be obtained by assuming the concentration of A_1 in the limit of zero electrolyte addition is given by α [surfactant concentration]. This exercise would provide an insight into the degree of dissociation of each surfactant species relative to the observed solution behavior but is complicated by a lack of knowledge of the true ionic strength and effective cmc at any point in the analysis. Such a problem could be avoided by the addition of the appropriate coun-

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terion, be it sodium 4-chlorobenzoate, sodium 3,4-dichlorobenzoate, or sodium 3,5-dichlorobenzoate.

Another point to note is that the surface potential of CTAC micelles obtained by a spectroscopic probe technique³³ and the theoretical surface potentials generated in the fitting exercise to the ζ potential data of Figure 3 show excellent agreement, within 10 mV. Such agreement is interesting since it reflects that the description of the interface in terms of the C_1 and C_2 parameters for this surfactant system is reasonable. The area per head group differences between the planar and micellar configurations are of significance in the assessment of the inner layer capacitance, but the changes are such that subtle rather than radical adjustments in C_1 are required. Therefore, this assessment gives greater credence to the chosen value of K_d . Similar spectroscopic probe data for the double alkyl chain quaternary ammonium surfactant salts (in vesicle form), although not available, would help considerably in elucidating the degree of binding in these systems. It would also help confirm whether significant counterion binding differences exist between surface and solution species of the same molecule.

Summary

1. The counterion binding of bromide and acetate ions to bilayers of the double alkyl chain surfactant DHDA and of various simple and complex counterions to the single alkyl chain surfactant CTA has been examined using a flat plate streaming potential technique.
2. The binding of Br^- ions to a DHDA bilayer shows electrokinetic behavior consistent with previous obser-

vations of a similar system as measured by the force balance technique.^{3,4}

3. The binding of acetate ions to a DHDA bilayer occurs but to a lesser extent than Br^- . This conclusion is not supported by previous direct force measurements on this system,³ but is in close accord with new work²⁸ which allows for the contribution of hydration forces to the overall force measurements.

4. In the limit of zero added electrolyte, the ζ potentials of the CTA salts studied show a dissociation equilibria with their counterions in the series $\text{Cl}^- \approx 4\text{-Cl} > 3,4\text{-Cl} > 3,5\text{-Cl}$. This is in agreement with solution conductivity studies. The data for CTAC are adequately described by a simple dissociation model as a function of added electrolyte if it is assumed that $\approx 94\%$ of the surfactant head groups are neutralized by the adsorption of counterions.

Acknowledgment. P.J.S. acknowledges receipt of an Australian Postgraduate Research Award and L.J.M. receipt of Grant CHE-8611586 from the National Science Foundation. The comments of Dr. D. Y. C. Chan and Prof. L. R. White on the modeling aspects of this work are gratefully acknowledged. We are also grateful to Prof. D. F. Evans for sending us a preliminary draft of a manuscript on new DHDA-mica direct force measurements.

Registry No. CTAC, 112-02-7; DHDA, 71326-37-9; DHDAB, 70755-47-4; CTA 3,5-dichlorobenzoate, 117932-67-9; CTA 3,4-dichlorobenzoate, 137003-28-2; CTA 4-chlorobenzoate, 61482-45-9.