

## Surfactant Adsorption at the Solid-Liquid Interface: Dependence of Mechanism on Chain Length

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At low concentrations, alkylammonium ions affect the  $\zeta$ -potential of quartz in nearly the same way as do sodium ions; at a certain concentration of alkylammonium ions there is a sudden change in the electrokinetic potential. This has been attributed to the formation of "hemimicelles" or two-dimension aggregates of the long-chain ions. As in micelle formation, the cohesive or van der Waals interaction between hydrocarbon chains reduces the work of bringing the polar groups together into aggregates at the solid-liquid interface. We have measured the  $\zeta$ -potential-concentration curves for quartz in the presence of alkylammonium acetates of chain length from 10 to 18 carbons. From the variation with chain length of the concentration of surfactant at zero  $\zeta$ -potential, it is possible to determine the value of the van der Waals cohesive energy. Our value of  $0.97kT$  or 580 cal./mole, in good agreement with literature values, substantiates the hemimicelle hypothesis and strengthens the validity of electrokinetic techniques.

### Introduction

In a previous publication,<sup>1</sup> evidence was presented for the occurrence of lateral interaction between hydrocarbon chains of alkylammonium ions adsorbed at the quartz-aqueous solution interface. It was concluded that in dilute solutions alkylammonium ions are adsorbed as individual ions; once the adsorbed ions reach a certain critical concentration at the solid-liquid interface, they begin to associate into two-dimensional patches of ions in much the same way as they associate into three-dimensional aggregates to form micelles in bulk solution. The forces responsible for this association at the surface will be the same as those operating in the bulk, except that coulombic attraction for the surface adsorption sites will aid the association.

Because of the proposed appearance of these adsorbed surfactant ions, the patches of associated ions have been termed "hemimicelles."<sup>2</sup> The critical concentration at which the association is observed is referred to as the hemimicelle concentration,  $C_{HM}$ , in moles/liter. Electrokinetic, adsorption density, contact angle, and flotation-rate data all show an abrupt change in behavior at the hemimicelle concentration. Such correlation of interfacial parameters has been demon-

strated for the system quartz-dodecylammonium acetate, both in terms of the pH effect<sup>3</sup> and in terms of the effect of the concentration of dodecylammonium acetate at fixed pH.<sup>4</sup> Contact angle studies by Zisman for the adsorption of amines and carboxylic acids on platinum<sup>5</sup> also suggest that lateral interaction between adsorbed surfactant species takes place at a certain critical concentration.

The adsorption isotherm of alkyl surfactants at the solid-water interface for such solids as silica and alumina, while not extensively investigated, does show a general pattern<sup>6-8</sup>; the isotherm consists of two regions which join at a distinct point which we have termed

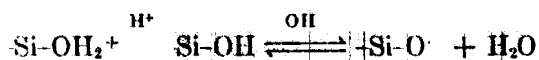
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the "hemimicelle concentration." Adsorption is more extensive for concentrations greater than the hemimicelle concentration. No quantitative description of the adsorption process has been presented that accounts for the break in the isotherm and the concomitant change in slope.

In the investigation reported in this paper, quantitative evidence of the occurrence of lateral interaction between adsorbed alkyl surfactant ions, i.e., hemimicelle formation at the solid-liquid interface, has been obtained from determinations of the effect of chain length on the electrokinetic potential of silica in aqueous solutions of alkylammonium acetates. Based on the Stern-Grahame model of the electrical double layer, it has also been possible to examine the range of application of  $\zeta$ -potential data and to use these data to interpret certain properties of adsorption isotherms for the system silica-dodecylammonium acetate at neutral pH.

### Theory

For the examination of the effects of surfactant species at solid-liquid interfaces, the following model of the electrical double layer will be applied. Hydrogen and hydroxyl ions are potential-determining ions for silica,<sup>9-11</sup> and the surface charge of silica might be considered to result from adsorption-dissociation of water molecules at broken silicon-oxygen bonds, depicted schematically as



Let the closest approach of positive counterions to this negative surface be at the plane distance  $\delta$  out from the surface. In accordance with the Stern-Grahame model, the diffuse layer charge can be expressed by the exact form of the Guoy-Chapman equation for the potential at plane  $\delta$ , i.e.,  $\psi_\delta$ . The diffuse layer charge, expressed as charge within a column out from the plane  $\delta$  and of unit area of cross section, is given by

$$\sigma_d = \sqrt{\frac{2\epsilon kT}{\pi}} \sqrt{n_0} \sinh\left(\frac{Ze\psi_\delta}{2kT}\right) \quad (1)$$

where  $\epsilon$  is the dielectric constant,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $Z$  is the valence including sign,  $e$  is the electronic charge, and  $n_0$  is the number of ions/cc. in the bulk. For 1-1 valent electrolytes, the adsorption density of positive counterions, expressed as moles/cm.<sup>2</sup> of surface at 25°, eq. 1 becomes

$$\Gamma_d^+ = 6.1 \times 10^{-11} \sqrt{C} [(\exp -19.46\psi_\delta) - 1] \quad (2)$$

where  $\psi_\delta$  is in volts and  $C$  is the bulk concentration in moles/cm.<sup>3</sup>.

Grahame's treatment of the compact double layer,<sup>12</sup> based on Stern's original concept,<sup>13</sup> leads to an expression for the adsorption of positive counterions at the plane  $\delta$ , which is of the form

$$\Gamma_d^+ = 2rC \exp(-W_\delta/kT) \quad (3)$$

where  $r$  is the radius of the adsorbed ion at the plane  $\delta$  and  $W_\delta$  is the work to bring the ion from the bulk of the solution up to the plane  $\delta$ . For the purposes of this paper it is unnecessary to subdivide the plane  $\delta$  into inner and outer Helmholtz planes as does Grahame in his detailed treatment of the double layer.<sup>12</sup>

The work  $W_\delta$  can be divided into electrostatic and chemical work terms, so that for cation adsorption

$$W_\delta = Z_+ e\psi_\delta - \phi \quad (4)$$

where for the case of adsorption of alkyl surfactants, such as dodecylammonium ion,  $\phi$  is the van der Waals energy in units of  $kT$  associated with removal of the alkyl chain from its aqueous environment. For an alkyl chain of  $n$  carbon atoms, assuming that

$$\phi/kT = n\phi'/kT$$

then  $\phi'$  is the van der Waals energy of interaction per CH<sub>2</sub> group between adjacent chains of adsorbed surfactant molecules. This interaction takes place at the bulk concentration referred to as the hemimicelle concentration,  $C = C_{HM}$ , by analogy to the critical micelle concentration of surfactant solutions. At surface coverages where this association between the chains takes place, the adsorption isotherm, for  $C > C_{HM}$ , is described by

$$\Gamma_d^+ = 2rC \exp(Z_+ e\psi_\delta + n\phi')/kT \quad (5)$$

Equations 3 in logarithmic form can be differentiated to give

$$\frac{d \ln \Gamma}{d \ln C} = \frac{d \ln \Gamma_d^+}{d \ln C} = 1 + \frac{dy}{d \ln C} + \frac{\phi'}{kT} \left( \frac{dn}{d \ln C} \right) \quad (6)$$

where  $\Gamma$  is the experimental value of the adsorption density and

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(13) O. Stern, *Z. Elektrochem.*, **30**, 508 (1924).

$$y = \frac{Z \cdot c \psi_\delta}{kT}$$

The differential ( $dn/d \ln C$ ) expresses the fact that the effective number of carbons that can be removed totally from an aqueous environment by hydrocarbon chain association increases as the surface coverage increases. At the  $C_{NM}$ , the effective value of  $n$  is zero; at a monolayer,  $n = 12$  for dodecylammonium acetate. That the effective value of  $n$  increases linearly with  $\ln C$  over this range has been verified by Fuerstenau and Modi for alkyl sulfates at the alumina-water interface.<sup>14</sup>

If after association of the alkyl chains the potential is reduced to zero, it follows from eq. 5 that

$$\ln C_0 = -n(\phi'/kT) - \ln (\Gamma_\delta^+)_0 - \ln 2r \quad (7)$$

where  $C = C_0$  at  $\psi_\delta = 0$ . If the ratio of the adsorption density at  $\psi_\delta = 0$  to the factor  $2r$  is relatively independent of chain length, then the natural logarithm of the concentration of alkyl surfactant ions at  $\psi_\delta = 0$  should be a linear function of the alkyl chain length with a slope equal to  $-\phi'/kT$ .

In obtaining the above equations, no simplifying assumptions have been made other than to assume the Stern-Grahame model of the double layer. The potential  $\psi_\delta$  is the potential of the Stern layer, and for successful use of eq. 6 and 7, an estimate of  $\psi_\delta$  is required. A convenient measure of the potential at plane  $\delta$  is the electrokinetic or  $\zeta$ -potential, defined as the potential at a plane (or layer<sup>15</sup>) at which shearing occurs within the double layer. We feel that  $\zeta$ -potential studies can be used to interpret these phenomena because (1) the potential difference between plane  $\delta$  and the shear plane is small compared to the total potential difference across the double layer, provided the ionic strength is less than about  $10^{-1} M$  and (2)  $\zeta$ -potentials, when expressed as a change in  $\zeta$  with respect to a change in some other parameter as illustrated by eq. 6, do in fact give agreement between theory and experiment. These agreements will be presented later in the paper. The following formal substitutions are suggested

$$\frac{d\psi_\delta}{d \ln C} \equiv \frac{d\zeta}{d \ln C} \quad (8)$$

in eq. 6, and in eq. 7

$$\left( \frac{d\psi_\delta}{dn} \right)_{\zeta=0} = 0 \quad (9)$$

Equation 9 can similarly be expressed as: at  $\zeta = 0$  (i.e., experimentally observed), there is no change in  $\psi_\delta$  with change in chain length of the adsorbed surface-

tant. If  $\psi_\delta = 0$ , then  $\zeta$  must be zero, and there is probably negligible error involved in assuming that at low ionic strengths  $\psi_\delta$  is zero when  $\zeta$  is zero.

## Experimental

Brazilian quartz,  $48 \times 65$  and  $28 \times 35$  mesh, was used in this investigation. It was prepared by leaching with concentrated hydrochloric acid, washing free of chloride ions, and then stored in distilled water. The alkyl amines were obtained from Armour Industrial Chemical Co., Chicago, Ill. All amines were dissolved in ether anhydrous, then added to the equimolar quantity of glacial acetic acid, and the acetate obtained was recrystallized from ether anhydrous, dried at room temperature in a desiccator, and stored in a cool place. The conductivity water used for making reagent solutions was prepared in a quartz still from laboratory distilled water. Conductivity was less than  $8 \times 10^{-7}$  ohm<sup>-1</sup> cm.<sup>-1</sup>. The water was stored and dispensed in a carbon dioxide-free atmosphere. All measurements were conducted at pH values ranging from 6.5 to 6.9.

The apparatus used for streaming potential studies<sup>16</sup> is based on the same principles and assembly described earlier with few modifications. The cell assembly mainly consists of a porous plug filled with  $48 \times 65$  mesh quartz particles. A layer of  $28 \times 35$  mesh particles placed at the two ends prevents any of the  $48 \times 65$  mesh particles from passing through the holes in the electrode. The potential developed is fed into an E-II Laboratory Model 215 electrometer, with an input impedance in excess of  $10^{14}$  ohms, and the output is fed to a Beckman recorder (Type 93500) through a Cahn recorder control. For measurements of resistance less than  $10^3$  ohms, a General Radio Co. (Type 1650-A) impedance bridge was used. For measurements of higher resistances, a precision resistor of resistance approximately equal to that of the test solution was placed in parallel with the electrodes. The resistance of the plug with the test solution is then given by the relation

$$R_1 = R_2 \frac{E_1}{E_2} \quad (10)$$

where  $R_1$  is resistance of plug with the test solution,  $R_2$  is the known resistance,  $E_1$  is the streaming potential without using  $R_2$ , and  $E_2$  is that with  $R_2$  in parallel. A correction for variation of dielectric constant of the

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medium with temperature, even though small, was made. The formula used in calculating  $\zeta$ -potentials after applying the correction is

$$[9.69 + 0.05(t - 25)] \times 10^4 \frac{E\lambda}{P} \text{ (mv)} \quad (11)$$

where  $\zeta$  is  $\zeta$ -potential in mv.,  $t$  is temperature of the solution in  $^{\circ}\text{C}$ .,  $E$  is the streaming potential in volts,  $P$  is the driving pressure in cm., and  $\lambda$  is the specific conductivity of the solution in  $\text{ohm}^{-1}\text{cm}^{-1}$ .

## Results

The  $\zeta$ -potential-concentration curves for quartz in the presence of long chain amines at pH 6.5-6.9 and at 22-25 $^{\circ}$  are given in Fig. 1 for alkyl chain lengths from 10 to 18 carbon atoms. Included in this figure is the  $\zeta$ -potential-concentration curve for quartz in the presence of ammonium acetate under the same conditions.

All alkylammonium ions change the sign of the  $\zeta$ -potential, but ammonium ion itself does not. The effect of increase in alkyl chain length is to lower successively the hemimicelle concentration, i.e., the bulk concentration at which van der Waals interaction takes place between adsorbed ions at the solid-liquid interface.

For comparison, the critical micelle concentrations for the alkylammonium acetates are  $C_0$ ,  $4 \times 10^{-2} M$ ;  $C_{12}$ ,  $1.3 \times 10^{-2} M$ ;  $C_{14}$ ,  $4 \times 10^{-3} M$ ;  $C_{16}$ ,  $8 \times 10^{-4} M$ ; and  $C_{18}$ ,  $3 \times 10^{-4} M$ . All major changes in the electrokinetic curves occur at concentrations far below the respective c.m.c. values.

## Discussion

The concentration  $C_0$ , at which the  $\zeta$ -potential is reduced to zero is plotted in Fig. 2 as a function of the alkyl chain length ( $n$ ) of the ammonium acetate. The linear relation between  $\log C_0$  and  $n$  as predicted by eq. 7 is verified; the slope of this line in terms of the van der Waals cohesive energy per  $\text{CH}_2$  group is  $0.97kT$  or 580 cal./mole. This value is in excellent agreement with values of  $\phi'$  determined from solubility data<sup>17</sup> or from studies of micelle formation as a function of alkyl chain length of monofunctional surfactants.<sup>18,19</sup> Values of  $\phi'$  determined from properties of surfactant solutions vary from 1.0 to  $1.1kT$ . That an acceptable value of  $\phi'$  has been obtained from this analysis is substantial evidence in favor of the hemimicelle hypothesis. It is the operation of this van der Waals interaction energy that is the fundamental postulate of the hemimicelle theory. It is significant that the value of  $\phi'$  obtained for hydrocarbon chain association at a solid-liquid interface is slightly less than the usual

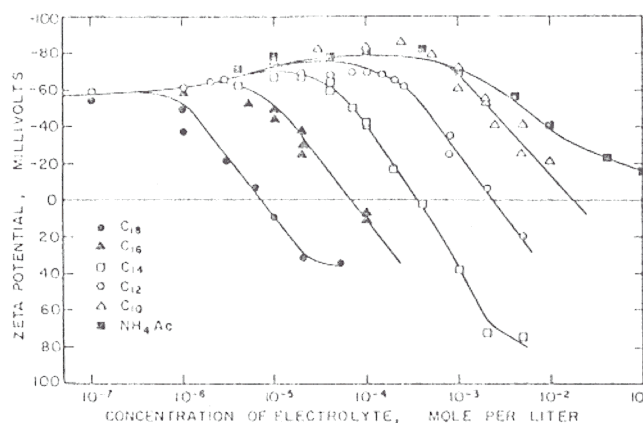


Figure 1. Effect of hydrocarbon chain length on the  $\zeta$ -potential of quartz in solutions of alkylammonium acetates and in solutions of ammonium acetate.

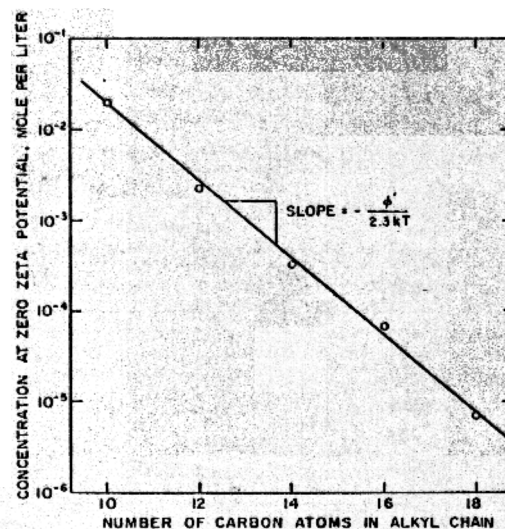


Figure 2. Variation of the concentration of alkylammonium acetate at zero  $\zeta$ -potential as a function of alkyl chain length.

value of 600-625 cal./mole deduced from micelle phenomena. This is probably due to the fact that complete association into a hydrocarbon liquid state is precluded on steric grounds for hemimicelles, since van der Waals interaction is restricted to two dimensions.

The observed linear relationship between the logarithm of the concentration of surfactant at  $\zeta = 0$  and the chain length (eq. 7 and Fig. 2) means that  $(\Gamma_{\delta}^+)_{\zeta=0}/2r$  is independent of chain length, where  $(\Gamma_{\delta}^+)_{\zeta=0}$  is the adsorption density of cations at plane  $\delta$  at  $\zeta = 0$  and  $2r$

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is the volume of charge at unit cross-sectional area through plane  $\delta$ . This finding implies that the electrostatic contribution to the energy of adsorption is located entirely within the charged polar head of the surfactant ion and is not affected by hydrocarbon chain association. Use of eq. 5, other than in differential form, would therefore require the value of the radius of the charged polar head group and not the "radius" of the whole surfactant molecule. A possible cancelling of the effect of  $(F_s^+)_0$  and  $2r$  should not be overlooked and will have to be evaluated in subsequent research.

Use of eq. 6 requires estimates of both the hemimicelle concentration and the concentration corresponding to monolayer coverage. Location of the hemimicelle concentration is partly obscured by the interference of surface conductance effects which, for example, are responsible for the maximum in the  $\zeta$ -log  $C$  data of Fig. 1. Surface conductance effects that are observed in streaming potential experiments on porous plugs are not observed if the experiments are carried out in capillary systems. The validity of the extrapolation of the alkylammonium curves up to the ammonium acetate curve to locate the hemimicelle concentration has been discussed by Davies and Rideal.<sup>20</sup>

The present electrokinetic data for the system quartz-dodecylammonium acetate leads to a value for the slope of the logarithmic adsorption isotherm for  $C > C_{HM}$  of approximately 2.5-3.0 to be compared with the experimentally determined value of 1.6-2.3.<sup>6</sup> The  $C_{HM}$  values obtained from the previous adsorption data and the present electrokinetic experiments are  $1.5 \times 10^{-4} M$  and approximately  $10^{-4} M$  DDA, respectively.

Notice that at low surface coverages before association of the alkyl chains, Guoy-Chapman theory, eq. 1, predicts a maximum limiting slope for the logarithmic adsorption isotherm of 0.5, but as the potential changes with concentration and approaches  $C = C_{HM}$ , the slope will become less than 0.5.

These agreements between the experimentally determined adsorption parameters and those deduced from  $\zeta$ -potentials with the aid of Stern-Grahame double layer theory are of considerable interest. Primarily, they strengthen the assumption of the equivalence between changes in  $\zeta$  and changes in  $\psi_\delta$  and, therefore, of the utility of electrokinetic results when analyzed in terms of differential quantities.

The above model of the adsorption process of alkyl surfactants can be considered appropriate for systems where the adsorption is purely physical adsorption. Alkylammonium ions on quartz fulfill this condition. Cases where the adsorption is clearly a chemisorption phenomena, where besides the van der Waals contribution to the work of adsorption there is a specific chemical interaction term, will require a more detailed treatment. Such systems as oleate on hematite appear to be of this category.

*Acknowledgments.* The authors wish to thank the National Science Foundation, Washington, D. C., for support of this work, and Armour Industrial Chemical Company for the high-purity amines used in this investigation.

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