Heat and Entropy of Adsorption and Association of Long-Chain Surfactants at the Alumina-Aqueous Solution Interface

by P. Somasundaran and D. W. Fuerstenau

Adsorption isotherms for dodecyl sulfonate on alumina were determined at 45°C and 25°C and the data was used for calculating the partial molar heat and entropy of adsorbed ions under various concentrations. Changes in $\Delta H$ and $\Delta S$ observed at certain concentrations agree with the postulate of interaction of surfactant ions to form two-dimensional aggregates at the solid-liquid interface. Values of the total $\Delta H$ and $\Delta S$ for the aggregation process calculated using the Clausius-Clapeyron equation is used to interpret the interactions of surfactant ions with each other as well as with the solvent molecules.

Froth flotation separations are sometimes conducted under conditions of relatively high or low temperature. It is known that the performance of these operations is dependent on the properties of various interfaces in the bubble-particle-solution system and these interfacial properties generally involve the adsorption of surfactants or collectors from solution. However, even though extensive applications have been made of thermodynamics to the adsorption of gases by solids, there has been very little thermodynamic study in the past on the adsorption from aqueous solution of collectors on minerals. A number of factors may be responsible for this. For example, unlike the adsorption of gases on solids, adsorption from solution is influenced by the solvent species in addition to the adsorbate species. Another problem is the possible variation of the surface charge of minerals as well as variation of hydration of adsorbate species with temperature.

In this investigation, we have made an attempt to study the thermodynamics of the adsorption of sodium dodecyl sulfonate on alumina. In our previous studies, adsorption isotherms of sodium dodecyl sulfonate on alumina were determined as a function of concentration and pH, and the data were interpreted in terms of a model wherein the surfactant ions are adsorbed as individual ions from dilute solutions, but when a certain critical concentration is exceeded, adsorbed ions interact with each other to form two-dimensional aggregates called hemimicelles at the interface. In the present study we have obtained information on the thermodynamic quantities of the hemimicelle association at the solid-liquid interface.

Theory

Adsorption of sodium dodecyl sulfonate on alumina can be explained on the basis of an electrical double layer model. The surface charge on alumina results from the interaction of $H^+$ and $OH^-$ with broken aluminum-oxygen bonds at the surface. The point of zero charge of alumina occurs at pH 9.1. Hence, for a system containing alumina particles in a dilute solution of an anionic surfactant in the neutral pH range, the electrical double layer will contain surfactant ions adsorbed at the interface as counter ions. At low concentrations, surfactant adsorption appears to occur by electrostatic attraction only. However, increasing the bulk concentration of the surfactant increases the adsorption to such an extent that interaction begins to occur among the hydrocarbon chains of the adsorbed surfactant ions at the interface. Correlation of various interfacial properties for the quartz-dodecylammonium acetate system and alumina-sodium dodecylsulfonate system has shown that marked changes in these parameters take place at a critical solution concentration.

The process of adsorption of dodecyl sulfonate ions, $X$, on alumina can be considered as follows:

$$X (\text{soln}, a = 1) \rightarrow X (\text{soln}, a = C_i)$$

$$\Delta G^* = RT \ln C_i$$

$$X (\text{soln}, a = C_i) \rightarrow X (\text{surf}, \Gamma)$$

$$\Delta G = 0$$

$$X (\text{soln}, a = 1) \rightarrow X (\text{surf}, \Gamma)$$

$C_i$ is the concentration of the sodium dodecylsulfonate in solution in mole per liter corresponding to an adsorption density 1 mole per sq cm at temperature $T_s$, and $(\Delta G^*_{X_i})_s$ is the relative partial molar free energy of the absorbed ions at this temperature. Here we have considered a solute standard state for $X$ in the solution such that the activity coefficient

$$\gamma_s \rightarrow 1 \text{ as } C \rightarrow 0.$$

Similarly at temperature $T_s$, the relative partial molar free energy of adsorbed ions will be

$$(\Delta G^*_{X_i})_s = RT \ln C_i.$$

Knowing $C_i$ and $C_s$ for the same adsorption density, one can evaluate $\Delta G^*_{X_i}$ at both temperatures, from which the heat and entropy terms involved in the adsorption process are calculated. $\Delta H^*_{X_i}$ and $\Delta S^*_{X_i}$ are the changes in heat content and entropy due to adsorption as well as dilution to the bulk concentration under consideration. Assuming ideal mixing and hence neglecting heat of

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dilution

\[ \Delta H^*_{x_e} = \Delta H^*_{x_{se}} = H_{x_e} - H^*_x \]  

(3)

where \( \Delta H^*_{x_{se}} \) is the change in partial molar heat content of sulfonate due to adsorption. \( H_{x_e} \) is the partial molar heat content of adsorbed ions related to total heat content of the surface \( (H^*) \) by

\[ H_{x_e} = \left( \frac{\partial H^*}{\partial T} \right) \]  

(4)

and \( H^*_x \) is the molar heat content of the surfactant in the standard state. The assumption that the heat of dilution in our case is negligible in comparison to the total heat of the process is probably valid but is subject to verification.

In the treatment of entropy terms, the contribution of entropy of dilution \( \Delta S_{21} \) to total \( \Delta S^*_{x_e} \) can be evaluated to obtain the entropy of adsorption using the following equation:

\[ \Delta S^*_{x_e} = \Delta S_{21} + \Delta S_{x_{se}} \]  

(5)

\[ = -R \ln C + S_{x_e} - S^*_{x_e} \]

\( \Delta S_{x_{se}} \) is the change in relative partial molar entropy of the sulfonate due to adsorption, \( S_{x_e} \) is the partial molar entropy of adsorbed ions related to total entropy of surface and \( S^*_{x_e} \) is the entropy of the surfactant ions in the standard state. Using Eq. 1, 2, and 3

\[ \Delta H^*_{x_{se}} = \frac{R (ln C_e - ln C)}{T - T_e} \]  

(6)

Similarly,

\[ \Delta S^*_{x_e} = \frac{R(T, \ln C_e - T, \ln C)}{T - T_e} \]  

(7)

and from Eq. 5

\[ \Delta S_{x_{se}} = \frac{R(T, \ln C_e - T, \ln C)}{T - T_e} - \Delta S_{21} \]  

(8)

By evaluating \( \Delta H^*_{x_{se}} \) and \( \Delta S^*_{x_{se}} \) as a function of the concentration, it is possible to get the changes in them due to such phenomena as hemimicellization. Adsorption in the system discussed here is complicated by the interaction of other components present. When sulfonate ions are adsorbed on alumina, in a system at constant ionic strength, they will be displacing anions of the supporting electrolyte from the double layer and possibly water molecules bound to the surface. For concentrations below the hemimicelle concentration, adsorption of sulfonate ions takes place by mere ion exchange. Since sodium chloride has been added during these experiments to maintain constant ionic strength in the system, adsorption of sulfonate ions below the hemimicelle concentration is accompanied by displacement of chloride ions from the surface. Alkyl sulfonate ions are considerably larger than chloride ions, and hence displacement of a relatively large number of water molecules from the "iceberg structure" on the surface may also take place when the surfactant is adsorbed. The changes in total thermodynamic quantities due to adsorption can therefore be expected to be different from the changes in the corresponding quantities for the adsorbed sulfonate ions only.

It is also possible to evaluate the thermodynamic quantities associated with hemimicelle formation by considering it as a phase change and using the Clusius-Clapeyron type equation:

\[ \frac{d \ln HMA}{dT} = -\frac{\Delta H_{21}}{RT^2} \]  

(9)

where \( HMA \) is the hemimicelle adsorption density and \( \Delta H_{21} \) is the heat of hemimicelle association at temperature \( T \). It is the adsorption density at hemimicelle formation that is used in Eq. 9 and not the bulk concentration. This is done so that we obtain thermodynamic quantities for the hemimicelle association only and not for the total process of adsorption and association at the solid-liquid interface.

In the case of micelles in bulk, a number of workers have considered the micelle to be a different phase from the aqueous solution and on this basis have treated micelle formation as a phase change. Recent experiments by Mysels and coworkers show that if proper experimental precautions are taken, the activity of the surfactant increases above the critical micelle concentration and that this increase can be explained with the help of a mass action model. It might, however, be noted that the increase in activity above micelle concentration is very small and treatments on the basis of a pseudophase separation model, even though not strictly correct, can yield useful information. For long alkyl chains, there is fair agreement between the mass action and phase separation models.

**Experimental Procedure**

Adsorption tests were carried out on Linde "A" alumina of 14.5 sq m per g surface area determined by measurements of adsorption of stearic acid from benzene and assuming 20.5A² for the stearic acid area. The sodium dodecylsulfonate used was prepared from dodecylsulfonate acid obtained from the Shell Development Co., Emeryville, Calif. The sodium salt obtained was purified by recrystallization from hot absolute ethyl alcohol. Triply distilled conductivity water was used for adsorption studies.

Adsorption of sodium dodecylsulfonate was determined at pH 6.9 and 25°C and 45°C by determining the difference in concentration of the surfactant in solution before and after adding alumina under equilibrium conditions. An atmosphere of purified nitrogen was maintained during the experiments. The ionic strength of the system was kept constant at 2 X 10⁻²M by adding a sufficient amount of 0.1M solution of sodium chloride. The sulfonate concentration was determined by the methylene blue method.

**Results and Discussion**

The adsorption isotherms of sodium dodecylsulfonate on alumina at pH 6.9 as a function of concentration of sulfonate at 25°C and 45°C is given in Fig. 1. These isotherms consist of three regions, which have been interpreted in terms of the electrochemical double layer theory elsewhere and will be mentioned only briefly here. At lower concentrations, sulfonate ions are adsorbed individually and adsorption takes place by an ion exchange mechanism. At the end of this region, the surfactant ions begin to associate and hemimicelles form. Here, adsorption results from electrostatic attraction plus the free energy decrease due to the association of hydrocarbon chains of adsorbed surfactant. When sufficient surfactant ions have been adsorbed to balance the surface charge, further increase in adsorption in the upper region results only from the van der Waals association between hydrocarbon tails. From Fig. 1 it can be seen that adsorption at all concentrations studied is lower at the higher temperature, in line with the past observations of physical adsorption on such adsorbents.
as carbon.\textsuperscript{44} Using Eq. 6, the partial molar heat content of the adsorbed surfactant ions has been calculated at various constant adsorption densities and is presented in Fig. 2. It is negative throughout the concentration range. Data of Fava and Eyring\textsuperscript{45} for detergent adsorption on cotton show similar results. However, by measuring the adsorption at one temperature and using the same sample and same solution for measurement at another temperature and calculating the heat of adsorption from the ratio of amounts adsorbed at two temperatures, the change in equilibrium concentration has been neglected by them. The partial molar entropy of adsorbed surfactant ions as calculated by Eq. 7 is given in Fig. 3 and the change in entropy as calculated by Eq. 8 is given in Fig. 4. Note that \(\Delta S_{\text{x,ads}}\) is negative throughout the entire range.

For adsorption only due to electrostatic attraction, it is reasonable that \(\Delta H\) is negative since the adsorption is analogous to ionic bond formation and there is no activation energy involved for the reaction. The entropy term suggests that there is a smaller entropy for the surfactant ions in the adsorbed state than in the solution, and this is because when the ions are adsorbed on the surface they have lesser number of degrees of freedom than they did in solution. Loss of translational entropy might partly be balanced by the configurational entropy of the surfactant ions on the surface and the presence of weak vibration perpendicular to the surface.\textsuperscript{44}

Continuous variations of the heat of adsorption with coverage have been reported by several workers as due to the heterogeneous nature of surfaces.\textsuperscript{45} In addition to such changes, we find some sharp changes in the values of \(\Delta H\) and \(\Delta S\) from Region 1 to Region 2 in accord with the postulate of hemimicelle formation. The contribution to \(\Delta H_{\text{x,ads}}\) due to hemimicelle formation is found to be of the order of +3 Kcal per mole and contribution to \(\Delta S_{\text{x,ads}}\) due to hemimicelle formation of the order of +4 e.u. (entropy units). Changes in \(\Delta H\) reported in literature for micelle formation exist in a wide range of +5 to -3 Kcal/mole.\textsuperscript{46,47,48}
processes to form micelles or hemimicelles involve reportedly destruction of the ordered water structure around a chain and the formation of hydrocarbon-hydrocarbon interactions, they should be endothermic in general. The magnitude of this effect should decrease with temperature in line with the findings of Jones and coworkers, Flockhart, Goddard and Benson, and Adderson and Taylor. The observed change in $\Delta S$ is due to the curved or bent hydrocarbon chain acquiring a more extended and flexible form in the hemimicelle.

The small decrease in entropy in the upper region is probably because increase in adsorption in that region takes place only by association and not by electrostatic attraction. Hence the effective number of adsorption sites is decreased. The fact that a minimum of absolute $\Delta S$ obtained in the two cases, that there is a further disordering in the system other than that of the surfactant ions. This can be explained on the basis of the water structure effects. Water molecules around the unassociated hydrocarbon chains have a relatively ordered arrangement. When the hydrocarbon chains associate, these water molecules will be free to become more disordered. It should be remembered that for each associating hydrocarbon chain there is more than one water molecule liberated from the vicinity of the chain so that, in total, the disordering is higher.

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Table 1. Configurational Entropy with Excess Entropy Values for Typical Concentrations

<table>
<thead>
<tr>
<th>Adsorption Density (Mole per Sq Cm)</th>
<th>Configurational Entropy</th>
<th>Excess Entropy</th>
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<tr>
<td>4</td>
<td>17.8</td>
<td>4.8</td>
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<tr>
<td>4</td>
<td>12.4</td>
<td>4.9</td>
</tr>
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<td>3.5</td>
<td>5.4</td>
<td>0.9</td>
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References
