Calorimetric Investigations on the Effect of Position of Functional Groups on Surfactant Adsorption

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The effect of the positions of sulfonate and of methyl groups on the aromatic ring of isomerically pure alkylxylenesulfonates on their adsorption investigated in this study using microcalorimetry and electrokinetic measurements is found to be marked. It was observed that the position of the sulfonate with respect to the alkyl chain is more critical than that of the methyl groups in determining the adsorption behavior. The surfactant with the sulfonate in the para position with respect to the alkyl chain adsorbed more than that with the sulfonate in the meta position. Steric constraint to the packing of the molecules is proposed to be the main reason for the differences in the adsorption of these surfactants. Zeta potential measurements showed no difference in the charge characteristics of the surfactants. Calorimetric results suggest enthalpy to be the main driving force for adsorption at low surfactant concentrations while the adsorption is entropy driven at higher surfactant concentrations.

EXPERIMENTAL

Materials

Alumina. Linde A alumina purchased from Union Carbide was used in this investigation. It is specified to be 90% alpha-alumina and 10% gamma-alumina and has a specific surface area of 15 m²/g as measured by a Quantasorb apparatus.

Inorganic reagent. NaCl used for regulating ionic strength was of A. R. grade.

Surfactants. 4C11 2,4-meta-xylenesulfonate (Meta), 4C11 3,5-para-xylenesulfonate (Para1) and 4C11 2,5-para-xylenesulfonate (Para2) used in this work were obtained from ARCO Oil and Gas Company. All the surfactants were specified to be at least 97% isomerically pure and were used as received. The structure of these surfactants are shown below:

INTRODUCTION

Adsorption of surfactants plays an important role in many industrial applications such as enhanced oil recovery, detergency, and flotation (1–3). An understanding of the mechanisms of adsorption is essential in improving the efficiency of the industrial processes.

Studies on surfactant adsorption have shown the phenomenon to be complex and to depend on a number of factors such as pH, ionic strength, temperature, and surfactant structure. Surfactant structure in particular plays an important role in adsorption as indicated by the effect of certain structural variations on adsorption (4–7). However, there exists no systematic work on the effect of position of functional groups on the aromatic ring of surfactants containing a benzene ring on adsorption. Using isomerically pure alkylxylenesulfonates, we have shown that the position of sulfonate influences markedly the micellization and adsorption properties of the surfactants (8).

In this work, we have examined the effect of the position of the sulfonate and also the effect of the position of the methyl groups on the benzene ring on the adsorption of isomerically pure alkylxylenesulfonates using microcalorimetry and electrokinetics.
Methods

Adsorption. A gram of alumina was conditioned in 5 cm³ of 0.03 kmol/m³ NaCl solution for 1 h at 43°C in a glass vial. Then 5 cm³ of the surfactant solution at the desired concentration was added to the slurry and the mixture conditioned for 24 h at the set temperature. After conditioning, solid–liquid separation was achieved using centrifugation at 3000 rpm for 10 min. A Beckman DU-8 UV-Vis spectrophotometer was used to analyze the surfactant at low concentrations and two phase titration (9) was used to analyze high surfactant concentrations. The absorbance was recorded at a wavelength of 254 nm.

Microcalorimetry. Calorimetric experiments were performed using a LKB 2107 differential microcalorimetry system. The calorimeter consists of a rotating block placed inside an air bath maintained at a constant temperature. The block consists of a sample cell and a reference cell. Each cell has two compartments. Mixing of the reactants is achieved by rotating the block. The heat of reaction is measured in terms of area. Area-heat calibration is then carried out by passing a known current for a set time period through a calibration heater in either one of the vessels. Three separate measurements in a narrow range around the reaction area are done for each experiment to obtain a calibration curve.

The heat of adsorption was measured by mixing the surfactant solution with the alumina slurry in the sample vessel and the same surfactant solution with same amount of diluent as in the alumina slurry in the reference cell. Two grams of alumina slurry with a solid to liquid ratio of 0.2 were used in the experiments. Since the same quantities of the surfactant and diluent were added in the two cells of the reference vessel, the heat of dilution of the surfactant solution is common to both the vessels and is cancelled from the signal. The dilution of the slurry itself was measured separately and subtracted from the reaction heat. The dilution effect arising from the release of dissolved species from alumina was eliminated by preparing the surfactant and the diluent in the supernatant of alumina conditioned at the set temperature in the experiments. Since the same quantities of the surfactant and the diluent were added in the two cells of the reference vessel, the heat of dilution of the surfactant solution is common to both the vessels and is cancelled from the signal. The dilution of the slurry itself was measured separately and subtracted from the reaction heat. The dilution effect arising from the release of dissolved species from alumina was eliminated by preparing the surfactant and the diluent in the supernatant of alumina conditioned at the system temperature and ionic strength. The heat of friction arising from the rotation of the blocks was very small (~10⁻⁷ cal) when compared to the heat of reaction (~10⁻³ cal). The friction heat was also subtracted from the reaction heat. The accuracy of the calorimeter was tested by measuring the enthalpy of dilution of NaCl solutions and the results are tabulated below in Table 1.

Electrokinetics. Zeta potential measurements were made with a Zeta Meter Model D system. The same samples used to measure adsorption were used to measure the zeta potential. The samples initially had a temperature of 43°C and after measurements dropped to 40°C.

RESULTS AND DISCUSSION

Adsorption

The adsorption isotherms for the three surfactants on alumina are given in Fig. 1. The shape of the isotherms of the three surfactants is typical of that for ionic surfactant adsorption on oppositely charged solids. The critical micelle concentrations (CMC) of the Paral, Paral2, and Meta under the experimental conditions are 3.3 × 10⁻⁴, 5.2 × 10⁻⁴, and 6.3 × 10⁻⁴ kmol/m³, respectively. The adsorption of the two para-xylenesulfonates is higher than that of the meta-xylene sulfonate in the premicellar region but is the same in the plateau region. The lower adsorption of the meta-xylene sulfonate in the hemimicellar region is due to

1. lower hydrophobicity of the alkyl chain due to higher inductive effect from the sulfonate, since it is closer to the alkyl chain in the case of meta-xylene sulfonate (4), and
2. higher steric constraints arising from the position of the sulfonate and methyl groups to the packing of the surfactant molecules in hemimicelles.

It can be seen that the two para-xylene sulfonates adsorb to the same extent. This suggests that the position of the methyl groups does not play as important a role as the position of the sulfonate. Also, it suggests that the higher steric hindrance to the packing of the molecules in the hemimicelles of meta-xylene sulfonate is due to the alkyl chain being closer to the sulfonate. Relative hydrophobicities of the para-xylene sulfonates and meta-xylene sulfonate were measured using reverse phase high performance liquid chromatography (11) and this indicated that the para-xylene sulfonates are more hydrophobic than meta-xylene sulfonate by 0.5 CH₂ group.

Zeta Potential Measurements

The lower adsorption of the meta-xylene sulfonate at low concentrations where the adsorption is considered to be due to electrostatic attraction between the mineral and the sulfonate is noteworthy. In order to understand this behavior, charge characteristics of the surfactants were determined by measuring the zeta potential. The zeta potential of alumina

<table>
<thead>
<tr>
<th>Cinit (mol/kg)</th>
<th>Cmeas (mol/kg)</th>
<th>ΔHads (cal/mol)</th>
<th>ΔHads (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.31</td>
<td>0.16</td>
<td>7.64</td>
<td>7.42</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2</td>
<td>15.2</td>
<td>16.9</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
<td>26.7</td>
<td>27.5</td>
</tr>
</tbody>
</table>

Note: The mean error is about 3%, thus there is good agreement between measured and literature values (10).
after adsorption of the three surfactants is shown in Figs. 2 and 3. It can be seen from Fig. 2 that the zeta potential with the para-xylene sulfonates is more negative than that with the meta-xylene sulfonate at all the concentrations. However, as seen from Fig. 3, when plotted as a function of the adsorption density, the zeta potential is the same for all the surfactants. Thus there seems to be no difference in the charge characteristics of the surfactants in the adsorbed layer. It is known that the water molecules near the alumina surface are structured, making the interfacial region relatively less hydrophilic than the bulk (12). It is possible that in addition to electrostatic attraction, some amount of the surfactant is also drawn to the interface by “hydrophobic” attraction. The para-xylene sulfonates being more hydrophobic are drawn to the interface more than the meta-xylene sulfonate leading to larger adsorption of the former.

**Calorimetry**

In order to better understand the mechanisms of adsorption, the adsorption enthalpies of the three surfactants were measured using calorimetry. Calorimetry has been used earlier to study the adsorption of surfactants at the solid/liquid interface (13-18) and is an useful tool to understand the interactions of the surfactant with the solid and also cooperative interactions between surfactants on the solid surface. The differential enthalpy of adsorption of the three surfactants as a function of adsorption density is shown in Fig. 4. The enthalpy of adsorption of the surfactants is exothermic at all adsorption densities. The enthalpy is constant and...
highly exothermic in a small range of low adsorption density. This can be interpreted as being due to the direct interaction between the ionic heads of the surfactant and the individual ionic sites of the surface. With increase in the adsorption density, the enthalpy decreases and finally attains a constant value. The adsorption density at which the enthalpy starts to decrease corresponds to the onset of formation of hemimicelles as inferred from the break in the adsorption isotherm; i.e., there is simultaneous interaction between the individual molecules and surface and between hydrophobic parts of the surfactant. Finally, when the adsorption proceeds purely due to hydrophobic interaction between the hydrocarbon tails, the enthalpy attains a constant value of about $-4 \text{ kcal/mol}$, which is of the same order of magnitude as the enthalpy of micellization of the surfactants ($\sim -1 \text{ kcal/mol}$). This indicates that like the formation of micelles, the formation of hemimicelles is also entropy driven. The error in the enthalpy at low adsorption densities (below $10^{-12} \text{ mol/cm}^2$) is 14% and at high adsorption densities is 3%.

The enthalpy of adsorption of the para-xylene sulfonates is higher than that of meta-xylene sulfonate at low adsorption densities suggesting greater attraction to the solid surface which results in their larger adsorption. This greater attraction as mentioned earlier is due to a combination of electrostatic and hydrophobic attraction of the surfactants to the interfacial region. Once the hemimicelles form, the adsorption enthalpy of the surfactants is similar. The free energy of adsorption with hemimelle formation was calculated using the equation (19)

$$\Delta G = RT \ln C_r,$$

where $C_r$ is the residual concentration of the surfactant in equilibrium at a particular adsorption density. The entropy of adsorption was then calculated by

$$\Delta G = \Delta H - T \Delta S.$$

The entropy of adsorption thus calculated for the para-xylene sulfonates and the meta-xylene sulfonate after the formation of hemimicelles is shown in Fig. 5. The probable error in the calculated entropy values is $\pm 3.5\%$. The entropy is higher and more positive for the para-xylene sulfonates than that for the meta-xylene sulfonate. The adsorption entropy can be considered to result from two contributions: a negative contribution from the ordering of the surfactant in the aggregate, and a positive and a major contribution from the release of the water molecules structured around the hydrocarbon tail upon its association (20). The tighter the packing of the molecules in the aggregates, the more the water molecules will be released and the higher the entropy. Thus, the higher entropy of the hemimicelle formation of the para-xylene sulfonates suggests a tighter packing of the molecules implying less steric hindrance to the formation of hemimicelles which was initially proposed as the reason for the higher adsorption of the para-xylene sulfonates. The calorimetric studies show that enthalpy is the main driving force for the adsorption of the surfactants at low adsorption densities while the adsorption is entropy driven at higher concentrations.

**SUMMARY**

The adsorption isotherms of the different alkylxylene sulfonates show a marked influence of the position of the sulfonate and the methyl groups on the benzene ring on their adsorption on alumina. The para-xylene sulfonates adsorbed an order of magnitude more than the meta-xylene sulfonate. The two para-xylene sulfonates adsorbed to the same extent, suggesting that the position of the sulfonate is more important than the position of the methyl groups in determining the adsorption characteristics. The lesser adsorption of the meta-xylene sulfonate was attributed to lower hydrophobicity of the alkyl chain and more importantly to the higher steric hindrance to the packing of the molecules in the hemimicelle. High performance liquid chromatography studies showed that the meta-xylene sulfonate is less hydrophobic than the para-xylene sulfonates by 0.5 CH$_2$ group. Zeta potential measurements showed the charge characteristics of the three surfactants to be similar. Microcalorimetric studies indicated that at low adsorption densities, enthalpy is the driving force for adsorption while at higher adsorption densities, entropy is the driving force. The adsorption enthalpy for the para-xylene sulfonates at low adsorption densities was greater than that of meta-xylene sulfonate suggesting greater attraction to the solid, resulting in higher adsorption. At high adsorption densities, the adsorption enthalpy is similar for the surfactants, but the adsorption entropy is higher for the para-xylene sulfonate.
lensesulfonates, indicating tighter packing of the molecules in the hemimicelles. Tighter packing of the molecules in the hemimicelles leads to higher adsorption of the para-xylenesulfonates.

Thus it is clear that the position of the sulfonate and the methyl groups on the aromatic ring of alkylxylenesulfonates has a major effect on the energetics of their adsorption and the nature of their aggregation at the interface leading to a marked effect on the extent of adsorption.

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REFERENCES