Surface and thermodynamic properties of linear alkyl benzene sulphonate and sodium lauryl sulphate in water

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The surface parameters, maximum surface excess, minimum area per molecule, surface pressure for linear alkyl benzene sulphonate and sodium lauryl sulphate in water have been calculated along with thermodynamic parameters from surface tension measurements. Micellization is favored both by energy effects as well as by entropy gain. The increase in critical micelle concentration with increase in temperature corresponds to the high symmetry of the system.

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Surface and thermodynamic parameters of surfactant in water and mixed aqueous solvent are of fundamental interest in the process of enhanced oil recovery1, detergency2,3 and solubilization4. These studies are also relevant in understanding the mechanism of inter molecular interactions5 in these systems and in biological process6. It is necessary to investigate these parameters in the light of environmental protection and catalytic biodegradable conditions7. At present LABS is the most commonly used surfactant for laundry products8, due to its biodegradable tendency with wide industrial applications. Keeping in mind the importance of surfactants an attempt has been made to determine the surface and thermodynamic parameters of LABS and SLS at two different temperatures.

Experimental

Deionised water was distilled twice with a small quantity of alkaline potassium permanganate. Then, water was distilled9 in a quick fit apparatus with sulphuric acid. The specific conductance of the distilled water prepared for the present study was in the order of < 2×10−6 Ω cm−1. Density measurements of solutions were made using pycnometer having capacity of 15 cm3. The pycnometer was calibrated with doubly distilled water having density 0.9972 g cm−3 and 0.9942 g cm−3 at 298 K and 308 K respectively10. Thermostatically controlled water bath (Tanco, Kanpur) capable of maintaining the temperature constant to ± 0.1°C was used during the studies. All weightings were made on a single pan digital balance (Citizen) with an accuracy of 0.0001 g. The density values were reproducible within ± 0.00002 g cm−3. The sensitivity of the pycnometer corresponded to a precision in density of 0.0001 g cm−3.

Surface tension measurements were made using a stalagmometer consisting of a pipette with a capillary outflow tube, the end of which was flattened out and polished in order to give a large dropping surface. The stalagmometer was calibrated using doubly distilled water and toluene having surface tension 73×10−3 N m−1 and 29×10−3 N m−1 respectively at 293 K. The necessary drop corrections were applied. The instrumental accuracy was ±0.0005 N m−1.

The LABS used in the study were obtained in the laboratory by sulphonation of linear alkyl benzene (IPCL, C10=14 C11=32 C12=37 C13=16 and C14 =1%) having an average molecular weight of 343. SLS was purchased from S.D. Fine Chem. Ltd. Surface tension measurements were made on an aqueous solution of LABS and SLS prepared by dissolving an accurately weighed sample in distilled water. No surface tension minima were found which implies that no surface active impurities exist in the studied LABS and SLS samples. The techniques employed for test of impurities was same as reported in literature11.

Experimental values of surface tension of LABS in the concentration range 6×10−5 mol m−3–24×10−4 mol m−3 and SLS in concentration range 2×10−5 mol m−3–12×10−4 mol m−3 at different concentrations are reported at two temperatures in Table 1.

Results and discussion

The experimental values of surface tension obtained at different concentrations of surfactant were used to obtained the critical micelle concentration (cmc) of the surfactant from the breakpoint of surface tension versus log [surfactant] plot. Surface pressure at cmc was calculated using the relation:
The experimental temperature range. The standard surface tension of surfactant solution in water of log versus surface tension. The minimum area per molecule calculated with the help of the following relation.

\[ A_{\text{min}} = 10^{14}/N \Gamma_{\text{max}} \]  

(3)

The surface excess, \( \Gamma_{\text{max}} \), depends upon the change in surface pressure, \( \pi \) surfactant solution relative to pure water. The standard Gibbs free energy of micellization is related to the cmc at any temperature by the following relationship

\[ \Delta G_{m}^0 = (2-p/n)RT \ln \text{cmc} \]  

(4)

It was assumed that \( \Delta G_{m}^0 \) values varies linearly in the experimental temperature range. The standard entropies and enthalpies for micellization were also calculated according to the relationships.

\[ \Delta S_{m}^0 = -\delta (\Delta G_{m}^0)/\delta T \]  

(5)

\[ \Delta H_{m}^0 = \Delta G_{m}^0 + T \Delta S_{m}^0 \]  

(6)

The value of \( p/n \) is the ratio of number of residual charges per micelle and the aggregation number. It was considered as unity for SLS and for LABS its value has been taken from literature. The value of cmc, surface pressure \( \pi_{\text{cmc}} \), surface excess \( \Gamma_{\text{max}} \), minimum area per-molecule \( A_{\text{min}} \), and thermodynamic properties of micellization, free energy \( \Delta G_{m}^0 \), entropy \( \Delta S_{m}^0 \) and enthalpy \( \Delta H_{m}^0 \) for both surfactants are presented in Table I.

The micellization takes place where the energy released as result of association of hydrocarbon chain of the monomer is sufficient to overcome the electrical repulsion between the ionic head group and decrease in entropy accompanying the aggregation. Therefore, in the study the increase in temperature results in an increase in cmc values because the kinetic energy of monomer has been raised. The lower value of cmc for LABS indicates that the hydrophilic end of LABS promotes the surface activity of molecule in comparison to SLS molecule due to the presence of benzene ring. The lower value of surface excess, \( \Gamma_{\text{max}} \), for LABS indicates that the molecules of LABS have greater tendency of shifting from liquid-air interface to the aqueous bulk phase. The surface pressure, \( \pi_{\text{cmc}} \), values were same for both surfactants and remained constant with increase in temperature. This implies that the solvent environment attains a similar stable state for micellization. The increase in the value of minimum area per molecule, \( A_{\text{min}} \), with increase in temperature for both the surfactants was observed due to the thermal agitation of the molecules.

The free energy of micellization includes all factors like chemical nature, size of surfactant moieties and other interactions between different phases present in the micellar solution. The calculation of free energy on the context of detailed molecular model was not possible from the observed experimental data. The calculated thermodynamic parameters, free energy and enthalpy, were negative and entropy was positive for micellization of both the surfactants in water. The minimal effect of temperature on the thermodynamic parameters indicates that the process of micellization

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Table I—The values of surface tension (\( \gamma \)), cmc, surface pressure (\( \pi_{\text{cmc}} \)), surface excess (\( \Gamma_{\text{max}} \)), minimum area per-molecule (\( A_{\text{min}} \)) and thermodynamic parameters, micellization free energy (\( \Delta G_{m}^0 \)), entropy (\( \Delta S_{m}^0 \)) and enthalpy (\( \Delta H_{m}^0 \)) for LABS and SLS

<table>
<thead>
<tr>
<th></th>
<th>LABS</th>
<th>SLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc ( \times 10^6 ) (mol m(^{-3} ))</td>
<td>( \gamma \times 10^3 ) (N m(^{-1} ))</td>
<td>( \gamma \times 10^3 ) (N m(^{-1} ))</td>
</tr>
<tr>
<td>300 K</td>
<td>320 K</td>
<td>300 K</td>
</tr>
<tr>
<td>0.6</td>
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<td>45</td>
</tr>
<tr>
<td>0.9</td>
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<td>42</td>
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<tr>
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<td>1.5</td>
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<td>36</td>
</tr>
<tr>
<td>1.8</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>2.1</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>2.4</td>
<td>34</td>
<td>34</td>
</tr>
</tbody>
</table>

\( \pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \)  

(1)

\( \Gamma_{\text{max}} = -(1/2.303 \text{ } \text{nRT}) \{\partial \gamma/\partial \log c\} \)  

(2)

The value of \( \{\partial \gamma/\partial \log c\} \) was obtained from the plot of log \( c \) versus surface tension. The minimum area per molecule of surfactant at liquid-air interface was also calculated with the help of the following relation.

\( A_{\text{min}} = 10^{14}/N \Gamma_{\text{max}} \)  

(3)

\( \Delta G_{m}^0 = (2-p/n)RT \ln \text{cmc} \)  

(4)

\( \Delta S_{m}^0 = -\delta (\Delta G_{m}^0)/\delta T \)  

(5)

\( \Delta H_{m}^0 = \Delta G_{m}^0 + T \Delta S_{m}^0 \)  

(6)
was spontaneous in nature. The equilibrium between monomeric phase and pseudo micellar phase was constant.

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References