

## Effect of Counterions on the Interfacial Tension and Emulsion Droplet Size in the Oil/Water/Dodecyl Sulfate System

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The effects of the size of counterions of anionic dodecyl sulfate surfactants on the interfacial tension and emulsion droplet size were investigated by the Wilhelmy plate method and optical microscopy. The size of nonhydrated counterions increases in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ . This order is reversed when these ions are hydrated by water due to the strongest hydration force of lithium ion. The largest size of hydrated  $\text{Li}^+$  resulted in the highest surface tension of surfactant solution, the highest interfacial tension at the hexadecane/surfactant solution interface, and the largest droplet size of emulsions in hexadecane/surfactant solution dispersions. These results were explained on the basis of area/molecule of surfactants at the interface which is influenced by the size of their counterions. The area/molecule of dodecyl sulfate (DS) with various counterions were in the following order:  $\text{LiDS} > \text{NaDS} > \text{CsDS}$ .

### Introduction

Ionic surfactants dissociate into ionic surface-active molecules and counterions when they are dissolved in water. These counterions significantly influence the properties of surfactant solutions, e.g., cmc (critical micelle concentration), micellar size, micellar catalytic activity, etc. The cmc in aqueous solution reflects the degree of binding of the counterion to the micelle. For aqueous systems, the increased binding of the counterions to surfactants causes a decrease in the cmc of the surfactant. The extent of binding of the counterion increases with an increase in the polarizability and valence of counterions and decreases with an increase in its hydrated radius.<sup>1</sup> Thus, in aqueous solution, for the anionic dodecyl sulfate (DS), the cmc decreases in the order  $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+$ . The cmc of LiDS, NaDS, and CsDS were reported to be 8.92, 8.32, and 6.09 mM at 25 °C by the measurement of specific conductance of solutions.<sup>2</sup> Missel, et al.<sup>3</sup> have reported that the micellar size is in the following order:  $R_h(\text{CsDS}) > R_h(\text{NaDS}) > R_h(\text{LiDS})$  at a given ionic strength, detergent concentration, and temperature. In general, the micellar catalysis is inhibited by counterions, and the larger the counterion, the greater the effect.<sup>4</sup> Also the ionized counterions perturb the local ordering or "structure" of water molecules. Several water molecules are bound to counterions due to ion-dipole interaction between counterions and water molecules.<sup>5</sup> As shown in Table I, the nonhydrated ion size follows the order of  $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$ , but the hydrated ion size comes in reverse order due to the greater hydration of a lithium ion compared to a sodium or cesium ion. The repulsive force between similar hydrated ions appears to increase on going from  $\text{K}^+-\text{K}^+$  to  $\text{Na}^+-\text{Na}^+$  to  $\text{Li}^+-\text{Li}^+$  (rather than the opposite as would be expected from the nonhydrated ion radii of these ions).<sup>5</sup> Therefore, the effectiveness of monovalent cations as coagulants decreases according to the so-called lyotropic series, viz.,  $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$  for monovalent ions.<sup>6</sup> The surface tension of surfactant solutions depends on the number of surfactant molecules at the surface. For a given surfactant, the greater concentration of surfactant molecules at the surface results in the lower surface tension.

In this study, the effect of the size of counterions of anionic dodecyl sulfate on the surface tension, interfacial tension at the hexadecane/water interface, and the emulsion droplet size of hexadecane and water mixtures were investigated. The surfactants studied are lithium dodecyl sulfate (LiDS), sodium dodecyl sulfate (NaDS), and cesium dodecyl sulfate (CsDS). Potassium

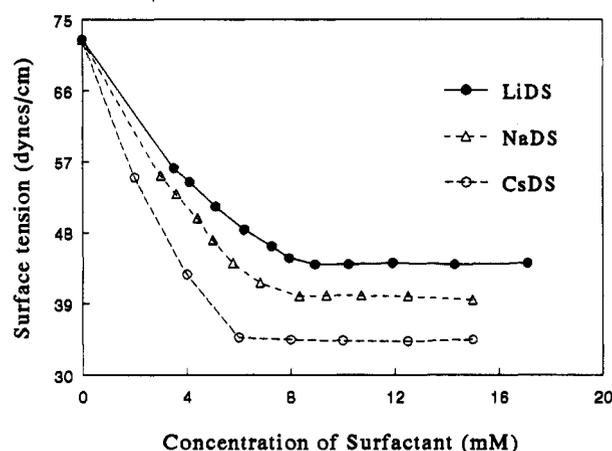


Figure 1. Surface tension of dodecyl sulfate at the air/water interface after foam fractionation.

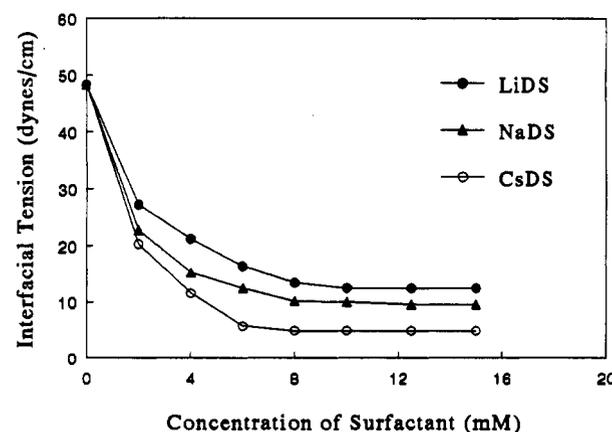


Figure 2. Interfacial tension of dodecyl sulfate at the hexadecane/water interface.

dodecyl sulfate (KDS) was not studied because micelles cannot be formed at 25 °C due to its higher Krafft point ( $\approx 30$  °C).

### Foam Fractionation of Surfactant Solutions To Remove Trace Impurities

LiDS (Kodak Co., 95%), NaDS (Sigma Co., 99%), and CsDS (synthesized according to the literature<sup>7</sup>) were purified by the

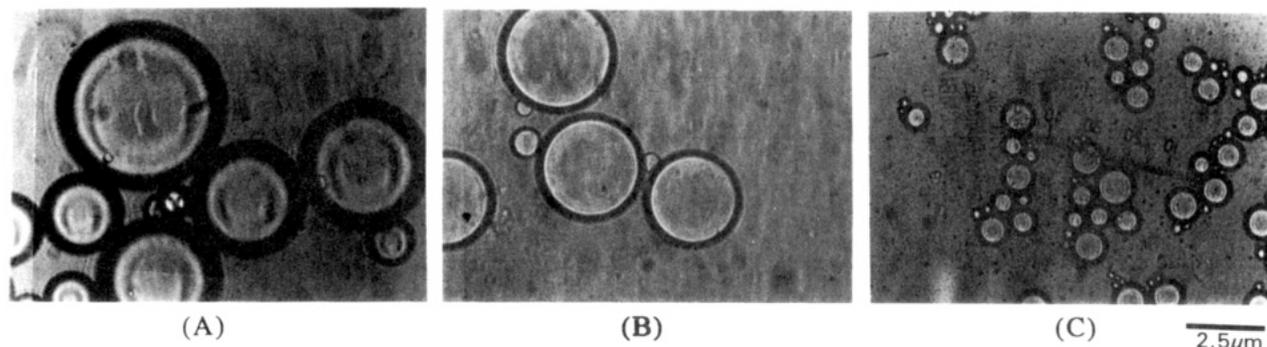


Figure 3. Emulsion droplet size in the mixture of hexadecane/50 mM surfactant solution: (A) LiDS, (B) NaDS, and (C) CsDS.

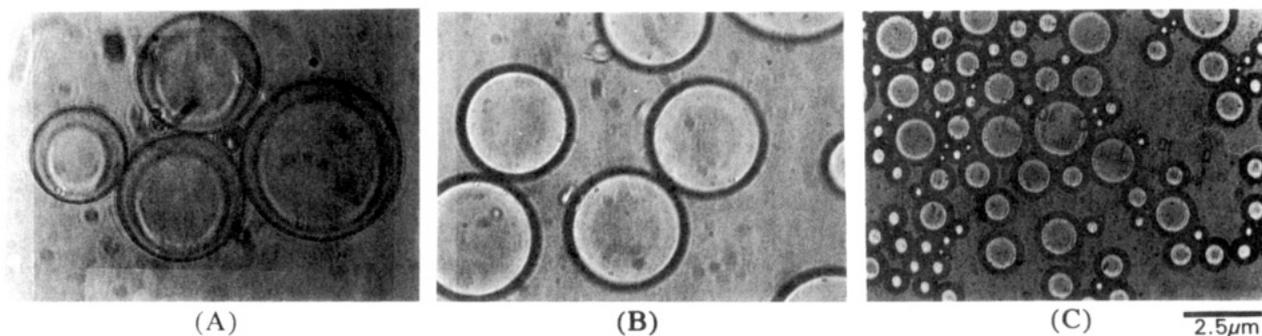


Figure 4. Emulsion droplet size in the mixture of hexadecane/100 mM surfactant solutions: (A) LiDS, (B) NaDS, and (C) CsDS.

foam fractionation method before use. When a surfactant exhibits a minimum in surface or interfacial tension, it is primarily due to trace impurities in the surfactant.<sup>8</sup> The removal of such impurities eliminates the minimum in surface or interfacial tension. The foam fractionation is one of the most efficient methods of removing the surface-active impurities from the surfactants. The trace impurities in the surfactant (e.g., dodecanol) partition in the foam when foam is generated in the solution.<sup>9</sup>

Air was blown into the surfactant solutions of 25 mM concentration in the column to make foam. Then the bottom solution was taken into another foam column. This procedure was repeated three times for each surfactant: 10 mL of solution was taken into the beaker after foam fraction. The water in the beaker was completely dried in the oven at 90 °C for 24 h to obtain the amount of surfactant in 10 mL of solution after foam fraction as recommended.<sup>10</sup>

### Experimental Section

The surface tension of LiDS, NaDS, and CsDS solutions was measured by a Rosano surface tensiometer (Biolar Corp.) using the Wilhelmy plate method. Doubly distilled water was used to prepare surfactant solutions. Also the interfacial tension between hexadecane and surfactant solutions was measured by the Wilhelmy plate method.

Hexadecane (4 mL) was added to 20 mL of surfactant solution of various concentrations and vigorously shaken with a vibrator for 30 s at a constant frequency of vibration to make the emulsion. Photographs of the emulsion droplets were taken through an optical microscope (Nikon, Japan) at 400 magnification just after the formation of emulsions to avoid the coalescence or flocculation of droplets.

### Results and Discussion

As shown in Figure 1, the surface tension of LiDS solution is higher than that of NaDS or CsDS solution. There was no surface tension minima near the cmc after foam fraction of surfactant. The interfacial tension between hexadecane and LiDS solution

TABLE I: Values for the Nonhydrated Ion Radius, Hydrated Ion Radius, Solvated Layer Thickness, and Solvation Volume of Each Ion

	nonhydrated ion radius (nm)	hydrated radius (nm)	solvation layer thickness (nm)	solvation vol (nm <sup>3</sup> )
Li <sup>+</sup>	0.068	0.38	0.312	0.230
Na <sup>+</sup>	0.095	0.36	0.265	0.195
K <sup>+</sup>	0.133	0.33	0.197	0.150
Cs <sup>+</sup>	0.169	0.33	0.161	0.150

TABLE II: Area/Molecule of Dodecyl Sulfate at the Air/Water Interface and the Surface Tension above the Cmc

	area/molecule (Å <sup>2</sup> /molecule)	surface tension above cmc (dyn/cm)
LiDS	61.3	44.2
NaDS	51.8	40.0
CsDS	44.8	34.4

was higher than that between hexadecane and NaDS or CsDS solution (Figure 2). This can be explained as follows.

The area/molecule at the interface of LiDS is larger than that of NaDS or CsDS molecules due to the larger size of hydrated counterions bound to the surfactant molecule as shown in Table I. The area/molecule at the interface can be calculated using the Gibbs adsorption isotherm:<sup>11</sup>

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{d \ln C} \quad (1)$$

where  $\Gamma$  is the concentration of surfactant at the interface,  $R$  is the gas constant,  $T$  is the temperature,  $\gamma$  is the interfacial tension, and  $C$  is the concentration of surfactant in the solution. The area/molecule at the interface can be calculated by dividing the film area by  $\Gamma$ . The area/molecule of each surfactant calculated by this equation at the air/water and oil/water interfaces is shown in Tables II and III. The area/molecule of LiDS was 61.3 Å<sup>2</sup> at the air/water interface compared to 51.8 Å<sup>2</sup> for NaDS and 44.8 Å<sup>2</sup> for CsDS. Also the area/molecule ratio of LiDS at the oil/water interface was larger than that of NaDS or CsDS.

An emulsification process needs energy to disperse one liquid into another liquid as droplets. The interfacial area dramatically

**TABLE III: Area/Molecule of Dodecyl Sulfate at the Hexadecane/Water Interface and the Interfacial Tension above the Cmc**

	area/molecule (Å <sup>2</sup> /molecule)	interfacial tension above cmc (dyn/cm)	av droplet size at 100 mM (μm)
LiDS	82.9	12.55	7
NaDS	68.9	9.65	5
CsDS	55.2	5.0	2.5

increases during the emulsification process. The work required ( $W$ ) to expand the interfacial area is given by<sup>12</sup>

$$W = \gamma(\Delta A) \quad (2)$$

where  $\gamma$  is the interfacial tension and  $\Delta A$  is the increase in the interfacial area. For constant  $W$ , a higher value of  $\gamma$  yields smaller  $\Delta A$ . Thus, the emulsion droplet size increases as the interfacial tension increases. Figures 3 and 4 show the droplet size of emulsion of LiDS/hexadecane, NaDS/hexadecane, and CsDS/hexadecane systems at 50 and 100 mM surfactant concentrations. The emulsion droplet size of the hexadecane/LiDS system was larger than that of hexadecane/NaDS or hexadecane/CsDS systems due to larger values of interfacial tension  $\gamma$  as explained in eq 2. The droplet sizes of emulsion at 50 mM surfactant concentration are smaller than those at 100 mM concentration. This is due to the effect of micellar lifetime. The lifetime of the micelles at 100 mM is longer than that at 50 mM for each surfactant. The more stable micelles cannot augment the flux of surfactant monomers to the rapidly expanding oil/water interface during the emulsification process.<sup>13</sup>

In conclusion, the number of LiDS molecules at the interface is less than that of NaDS and CsDS due to the larger hydrated

lithium ion. The largest hydrated counterion size of Li<sup>+</sup> in LiDS resulted in the highest surface tension of solution (Figure 1), the highest interfacial tension between the hexadecane/water interface (Figure 2), and the largest emulsion droplet size of oil/water mixtures (Figures 3 and 4) compared to NaDS and CsDS surfactants.

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