

## Krafft Temperature and Micelle Ionization of Aqueous Solutions of Cesium Dodecyl Sulfate

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The Krafft temperature of the surfactant cesium dodecyl sulfate, as determined by conductivity measurements, was shown to be a function of the  $\text{Cs}^+$  concentration in the aqueous phase whether the counterions are provided by the surfactant or both the surfactant and added  $\text{CsCl}$ . It is suggested that measurements of the Krafft temperature may form the basis to determine the degree of counterion dissociation in ionic micelles.

It has been generally accepted for many years<sup>1</sup> that micelles formed from ionic surfactants are charged because only a fraction,  $1 - \alpha$ , of the counterions are condensed onto the micelles, where the fraction of counterions dissociated from the micelles is denoted by  $\alpha$ . If counterions are added in the form of salt, then both surfactant and salt contribute to the concentration of counterions in the aqueous phase,  $C_{\text{aq}}$ . If the concentration of added salt is denoted by  $C_{\text{ad}}$ , standard mass balance arguments<sup>2–5</sup> show that  $C_{\text{aq}}$  is given as follows:

$$C_{\text{aq}} = F(S_{\text{t}})\{\alpha S_{\text{t}} + (1 - \alpha)S_{\text{f}} + C_{\text{ad}}\} \quad (1)$$

In eq 1,  $S_{\text{t}}$  is the total surfactant concentration and  $S_{\text{f}}$  the surfactant concentration in monomer form. All concentrations in this paper are given in moles per liter. The factor within the brackets would give the concentration of counterions in the aqueous phase if that phase occupied the entire sample; however, at higher surfactant concentrations, the excluded volume effect becomes important.<sup>4</sup> We correct approximately for this excluded volume effect by including the factor  $F(S_{\text{t}})$ .<sup>4,5</sup>

$$F(S_{\text{t}}) = \frac{1}{1 - VS_{\text{t}}} \quad (2)$$

where  $V$  is the molar volume of the anhydrous surfactant in liters per mole, assuming that the density of the surfactant is approximately 1.0 g/mL.<sup>4</sup>  $V = 0.398 \text{ L mol}^{-1}$  for cesium dodecyl sulfate ( $\text{CsDS}$ ). See ref 5 and references therein for a detailed discussion of eqs 1 and 2. The physical content of eq 1 is that any property dependent upon  $C_{\text{aq}}$  may be varied by changing either surfactant or salt concentrations. Many combinations of  $S_{\text{t}}$  and  $C_{\text{ad}}$  lead to the same value of  $C_{\text{aq}}$ , thus any property that is a function of  $C_{\text{aq}}$  will attain the same value for all of these combinations.

In many cases,  $\alpha$  is approximately constant.<sup>5,6</sup> In this case, a property may be demonstrated to depend only on  $C_{\text{aq}}$  by showing that it forms a common curve when plotted versus the quantity  $F(S_{\text{t}})\{\alpha S_{\text{t}} + C_{\text{ad}}\}$ , when either  $S_{\text{t}}$  and/or  $C_{\text{ad}}$  are varied. This fact follows because the value of  $S_{\text{f}}$  in eq 1 is the same for a given value of  $C_{\text{aq}}$ .<sup>5</sup> The hypothesis was recently advanced<sup>5</sup> that the aggregation number of an ionic micelle is one such property

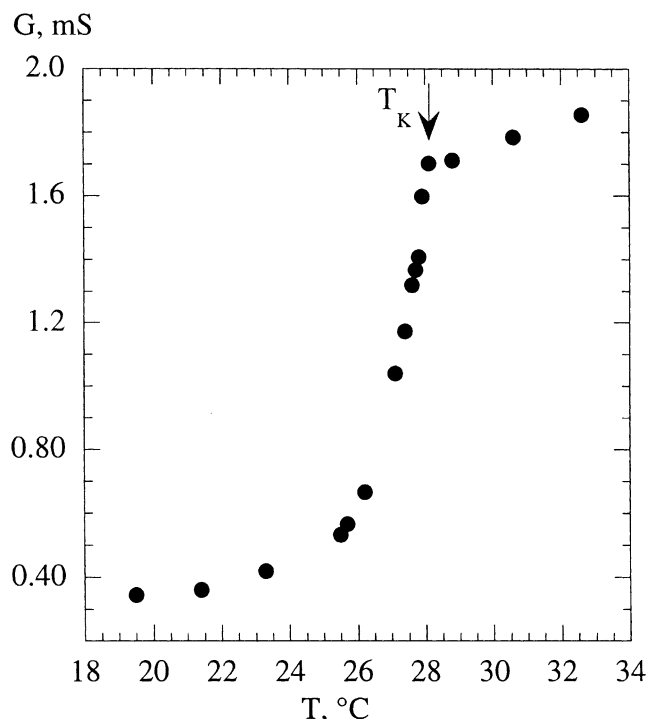
that is a function of  $C_{\text{aq}}$ . The purpose of this paper is to demonstrate that the Krafft temperature,  $T_{\text{K}}$ , of  $\text{CsDS}$  is another. An important consequence of the fact that a property is a function of  $C_{\text{aq}}$  is that the property is independent of the concentration of micelles at a given value of  $C_{\text{aq}}$ .

$\text{CsDS}$  was prepared by ion exchange, using a strong cation ion-exchange resin (Merck type 1), from sodium dodecyl sulfate ( $\text{SDS}$ , purchased from Touzart Matignon (France) and recrystallized twice from ethanol). A column of resin contained in a glass tube was first rinsed with a solution of  $\text{SDS}$ , put in the acid form, thoroughly rinsed with distilled water, neutralized by  $\text{CsOH}$  (Fluka), and rinsed again with deionized water until complete removal of any remaining excess base. The capacity of the ion-exchange resin used was 2–3 times larger than the amount of sodium ion to be exchanged. A 5 wt % solution of  $\text{SDS}$  was passed through the column of ion-exchange resin. The surfactant was obtained as a white powder by freeze-drying the ion-exchanged solution.

To determine  $T_{\text{K}}$ , weighed quantities of  $\text{CsDS}$  and water or water plus  $\text{CsCl}$  were heated to 40 °C to form clear solutions of known concentrations. These solutions were placed in a refrigerator at 5 °C for 24 h. Precipitation of  $\text{CsDS}$  occurred rapidly. The temperature of the precipitated system was slowly increased under constant stirring and its conductance was measured by using an autobalanced Wayne-Kerr conductivity bridge type B905. The temperature was measured with a thermocouple immersed in the investigated system. Figure 1 shows a typical curve of conductance versus temperature for  $[\text{CsDS}] = 51.6 \text{ mM}$  and  $[\text{CsCl}] = 0$ , where the square brackets indicate molar concentrations. Recall that at the approach of  $T_{\text{K}}$  the solubility of the surfactant and thus the conductance of the system increase very rapidly.<sup>6</sup> The Krafft temperature was taken as the temperature where the conductance vs temperature plot showed a break (see Figure 1). This temperature was the same as that corresponding to a complete clarification of the system, i.e., complete solubilization of the solid surfactant, within the precision of the thermocouple (0.1 °C). The relative values of  $T_{\text{K}}$  are estimated to be reproducible to  $\pm 0.2$  °C.

The conductivity of aqueous solutions of  $\text{CsDS}$  in the absence of salt was measured as a function of  $S_{\text{t}} = [\text{CsDS}]$  to determine the value of the critical micelle concentration in the absence of salt,  $\text{cmc}_0$ . From these same measurements, the value of  $\alpha$  was

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**Figure 1.** Conductance,  $G$ , versus temperature for a mixture of CsDS and water. The Krafft temperature, at the position of the sharp break labeled  $T_K$ , is the point at which the system clarified, forming a solution of concentrations  $[\text{CsDS}] = 51.6 \text{ mM}$  and  $[\text{CsCl}] = 0$ .

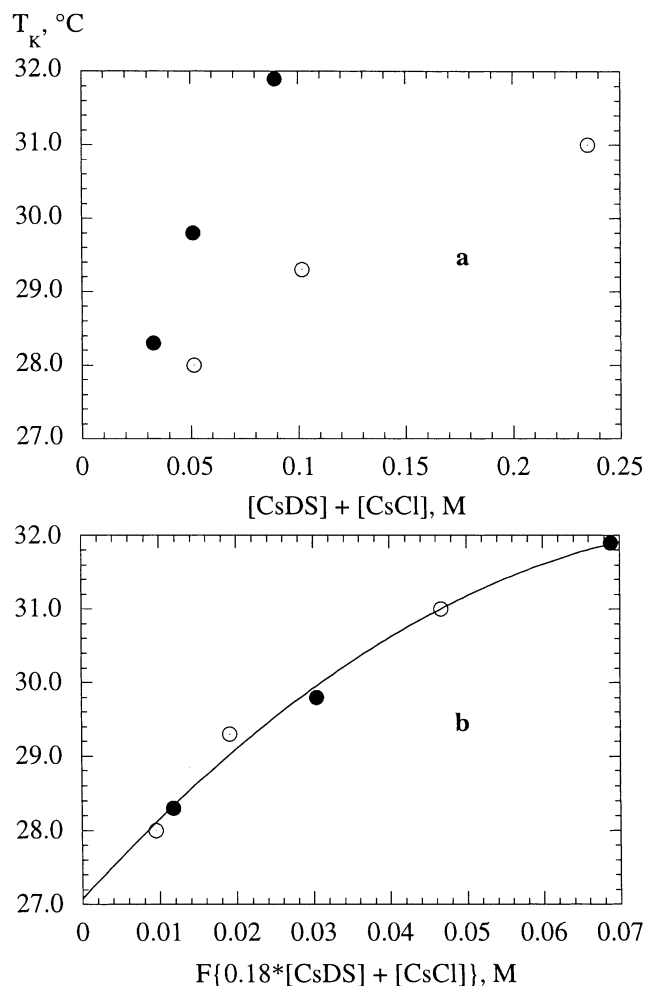
**TABLE 1: Values of  $\text{cmc}_0$  and  $\alpha$  for CsDS Micelles**

temp, °C	$\alpha$	$\text{cmc}_0$ , mM	$N^0$
30	0.18	6.2	78
40	0.18	6.4	68

estimated by employing the method of Evans.<sup>7</sup> The results are given in Table 1. The aggregation numbers at the cmc,  $N^0$ , needed in Evans' method<sup>7</sup> were determined by extrapolating to the cmc the aggregation numbers obtained from time-resolved fluorescence quenching.<sup>8–12</sup> These are tabulated in Table 1. These results were discovered quite by accident while carrying out experiments designed to characterize CsDS micelles as reaction media.<sup>13</sup> We noticed that samples left at room temperature above a certain value of  $C_{\text{aq}}$  had precipitated even though they contained different surfactant and salt concentrations.

$T_K$  was measured as a function of  $[\text{CsDS}]$  up to  $[\text{CsDS}] = 235 \text{ mM}$  in the absence of added CsCl and as a function of  $[\text{CsCl}]$  at constant  $[\text{CsDS}] = 26 \text{ mM}$ . Figure 2a shows  $T_K$  versus  $[\text{CsDS}] + [\text{CsCl}]$ . The Krafft temperature increases with either  $[\text{CsDS}]$  or  $[\text{CsCl}]$ . Figure 2b shows these same data plotted versus  $F\{\alpha[\text{CsDS}] + [\text{CsCl}]\}$  with the value of  $\alpha$  assumed to be independent of the temperature and  $C_{\text{aq}}$  with  $\alpha = 0.18$  (Table 1). Values of  $\alpha$  are often weakly temperature dependent;<sup>14</sup> however, in this case we are unable to detect a difference over the range  $T = 30\text{--}40 \text{ }^\circ\text{C}$ . That  $\alpha$  is constant with respect to  $C_{\text{aq}}$  is in accord with theory<sup>6,15</sup> and is often observed experimentally.<sup>5,6</sup> For example, for sodium dodecyl sulfate, it was recently shown that  $\alpha$  is constant up to a rather high concentration of 600 mM.<sup>5</sup> The solid line is a least-squares fit to all of the data using a quadratic trial function. The fact that all of the data fall on a common curve in Figure 1b shows that  $T_K$  is a function of  $C_{\text{aq}}$  only.

The Krafft behavior is usually discussed as an interplay between the solubility of the surfactant and the cmc.<sup>6</sup> Since the



**Figure 2.** Krafft temperature as a function of (a) the total concentration of surfactant and salt and (b) the quantity  $F(S_0)\{\alpha[\text{CsDS}] + [\text{CsCl}]\}$  with  $\alpha = 0.18$ . The open symbols are for salt-free solutions. The fact that the points form a common curve in (b) shows that  $T_K$  is a function of the counterion concentration in the aqueous phase, eq 1, whether the counterions are provided by the surfactant or both the surfactant and the salt.

solubility increases dramatically with temperature while the cmc does not, a temperature is reached when the solubility is equal to the cmc and micelles can form.<sup>6</sup> The temperature at which the solubility and cmc curves intersect is often called the Krafft point. As is common, we have taken  $T_K$  to be the temperature at which all of the surfactant is dissolved as indicated in Figure 1. Generally,<sup>6</sup> salt addition raises  $T_K$  as is observed here for CsDS. The novelty of these new findings is that surfactant addition also raises  $T_K$  in a quantitatively predictable manner given by eq 1.

There is no reason to believe that the result in Figure 2 would not be general for ionic surfactants. If further work shows this to be true; i.e., that  $T_K$  is a function of  $C_{\text{aq}}$ , then the Krafft temperature would provide another independent means to determine values of  $\alpha$ . The procedure to determine  $\alpha$  from measurements of properties that are a function of  $C_{\text{aq}}$  is described in recent papers,<sup>5,16,17</sup> which may be consulted for details. Briefly, any property that is a function of  $C_{\text{aq}}$  is measured as a function of  $S_t$  and  $C_{\text{ad}}$ . For equal values of the property, eq 1 yields equal values of  $C_{\text{aq}}$  from which the value of  $\alpha$  may be obtained. The approach is of interest because the value of  $\alpha$  is independent of the experimental technique and does not require an assumption on the dividing line between counterions being associated with the micelle or not.<sup>5,16,17</sup> The method has been

applied to sodium dodecyl sulfate using electron spin resonance (micelle hydration),<sup>5,16</sup> time-resolved fluorescence quenching (aggregation numbers),<sup>16</sup> and small-angle neutron scattering (aggregation numbers)<sup>16</sup> and to cationic micelles using electron spin resonance<sup>17</sup> and time-resolved fluorescence quenching.<sup>17</sup> In the previous sentence, the property measured is indicated in the parentheses. Note that the value of the aggregation number is not needed in the technique. The experiment need only ensure that the value of the aggregation number is the same for two samples.

Thus the Krafft temperature could be added to the growing list of properties that could be used to derive values of  $\alpha$ . We have employed the relatively easy experimental technique of conductivity; however, any technique ought to work. The approach could be applied to all ionic surfactants with experimentally accessible Krafft temperatures.

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