ARTICLES

Estimate of the Ionization Degree of Ionic Micelles Based on Krafft Temperature Measurements

Carolina Vautier-Giongo and Barney L. Bales*

Department of Physics and Astronomy and The Center for Supramolecular Studies, California State University, Northridge, California 91330-8268

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The Krafft temperature, \( T_K \), of two classical ionic surfactants, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), were measured by conductivity, in the absence and in the presence of added salt, to test a recent suggestion (J. Phys. Chem. B 2002, 106, 9033) that \( T_K \) measurements can be used to estimate the degree of counterion dissociation of ionic micelles, \( \alpha \). The method is based on the fact that \( T_K \) of SDS and CTAB are functions of the concentration of counterions in the aqueous phase, \( C_{aq} \), whether the counterions are provided by the surfactant or both the surfactant and added salt. The values of \( \alpha \) are estimated by requiring that the values of \( T_K \) fall on a common curve when plotted against any function of \( C_{aq} \) and are found to be in good agreement with the literature. The present results confirm that the Krafft temperature of ionic surfactants is one of the properties from which \( \alpha \) can be derived for both anionic and cationic micelles. In the case of SDS, because the aggregation number, \( N \), is known as a function of \( C_{aq} \), \( T_K \) may be plotted versus \( N \). The plot showed excellent linear correlation; however, it is not yet known if the linear behavior is theoretically significant.

Introduction

A definition of the degree of counterion dissociation, \( \alpha \), based on the variation of any micellar property that is a function of the concentration of counterions in the aqueous phase, \( C_{aq} \), has been previously proposed.1 The validity of this definition1 was demonstrated for properties such as the aggregation number, \( N \), and the micelle hydration as measured by EPR.1,2 A recent paper1 presented data consistent with the Krafft temperature being another such property that is a function of \( C_{aq} \) for cesium dodecyl sulfate (CsDS) aqueous solutions.

The concentration of counterions in the aqueous phase, \( C_{aq} \), according to the conventional pseudopotential ionic exchange mass balance relationship1–6 is given by

\[
C_{aq} = F(C_t)\{\alpha C_t + (1 - \alpha)C_f + C_{ad}\} 
\]  

(1)

where \( C_t \), \( C_f \), and \( C_{ad} \) are the molar concentrations of total surfactant, surfactant in monomer form, and added common counterion in the form of salt, respectively. 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 and can be corrected by including the factor \( F(C_t) \)

\[
F(C_t) = \frac{1}{1 - VC_t} 
\]  

(2)

where \( V \) is the molar volume of the anhydrous surfactant in \( \text{mol}^{-1} \), assuming that the density of the surfactant is approximately 1.0 g \( \text{mL}^{-1} \).6

According to eq 1, any property dependent upon \( C_{aq} \) may be varied by changing either surfactant or salt concentrations. Several combinations of \( C_t \) and \( C_{ad} \) will lead to the same value of \( C_{aq} \); thus, any property that is a function of \( C_{aq} \) will attain the same value for all of these combinations. Assuming that \( \alpha \) is constant with \( C_{aq} \), it is possible to demonstrate that a property depends only on \( C_{aq} \) by showing that it forms a common curve if plotted versus \( F(C_t)\{\alpha C_t + C_{ad}\} \), as follows

\[
F(C_t)\{\alpha C_t + C_{ad}\} = \text{constant} 
\]  

(3)

when either \( C_t \) or \( C_{ad} \) are varied and an adequate value of \( \alpha \) is employed, because the value of \( C_t \) in eq 1 is the same for a given value of \( C_{aq} \). The procedure of eq 3 is valid whether \( \alpha \) is constant or if it varies as a function of \( N \). There is experimental1,7 evidence that \( \alpha \) remains nearly constant as \( C_t \) or \( C_{ad} \) is varied, at least in the range of surfactant and added salt concentrations where the micellar growth is slow.7a Nevertheless, \( \alpha \) can change considerably due to changes in the micellar shape.6,8 Thus, in this work, we deal with \( C_t \) and \( C_{ad} \) in the range below the sphere-to-rod transition. Theoretically,9 \( \alpha \) is also found to be approximately constant. In addition, \( \alpha \) shows only a weak dependence with the temperature.10 Therefore, we proceed assuming that \( \alpha \) is constant. An important consequence of the fact that a property is a function of \( C_{aq} \) is that the property is independent of the concentration of micelles at a given value of \( C_{aq} \). For a detailed discussion of eqs 1 and 2, see ref 2 and the references therein.

In our recent work, we suggested that the Krafft temperature measurements for ionic micelles might be used to estimate the...
degree of counterion dissociation of CsDS. The objective of the present work is, first, to show that the increase in Krafft temperature with the addition of the counterions for other surfactants, both anionic and cationic, is a function of $C_{\text{vap}}$ as given by eq 1, and, second, to estimate the values of $\alpha$ for these surfactants. For this purpose, we used conductivity measurements to determine Krafft temperatures of aqueous solutions of two classical ionic surfactants that have accessible Krafft temperatures, the anionic sodium dodecyl sulfate (SDS) and the cationic cetyltrimethylammonium bromide (CTAB).

**Experimental Section**

**Materials.** Sodium dodecyl sulfate (SDS; Sigma) and cetyltrimethylammonium bromide (CTAB, Aldrich), as well as analytical reagent grade sodium chloride (Fisher) and sodium bromide (Alfa Aesar), were used without further purification. The electrical conductance of the distilled and deionized water (NANOpure) used was less than 1 $\mu$S at 25°C.

**Krafft Temperature Measurements.** To determine $T_K$, clear aqueous solutions of surfactant, SDS or CTAB, in the absence or in the presence of salt of a common counterion (NaCl for SDS and NaBr for CTAB) were prepared and placed in a refrigerator at c.a. 5°C for at least 24 h, where the precipitation of surfactant hydrated crystals occurred. The temperature of the precipitated system was raised gradually under constant stirring, and its conductance ($G$) was measured using an autobalance Wayne-Kerr conductivity bridge 6430A and a Radiometer Analytical conductivity cell. At each temperature, the conductance reading was checked every 2 min until it reached a steady value. The temperature was measured using a thermocouple (precision of $\pm 0.01$ °C) immersed in the investigated system. The Krafft temperature was taken as the temperature where the conductance versus temperature plots showed an abrupt change in slope, as indicated by the arrows in the curves presented in Figure 1. Operationally, $T_K$ values were determined from plots of the second derivative of the data. This temperature was the same as that required to completely dissolve the hydrated solid surfactant, judged visually to be the point of complete clarification of the system. The reproducibility of $T_K$ measurements on a single sample (typically $\pm 0.05$ °C) was superior to the reproducibility in samples presumably prepared identically (averages about $\pm 0.1$ °C). It is important to distinguish between our definition of $T_K$ and the Krafft point, $T_K$, which is defined to be the temperature at which the solubility of the monomer becomes equal to the critical micelle concentration, cmc. Above the Krafft point, micelles begin to form provoking a rapid increase in the solubility of the surfactant as was first clearly described by Murray and Hartley in 1935.

**Results**

For SDS, $T_K$ was measured as a function of [SDS]$_t$ up to [SDS]$_t = 600$ mmol L$^{-1}$ in the absence of added NaCl. In the presence of NaCl, the maximum [SDS]$_t$ used was 250 mmol L$^{-1}$ and the maximum [NaCl] was 60 mmol L$^{-1}$. Under these conditions, it was shown previously that $\alpha$ is constant for SDS. For CTAB, the measurements were performed using [CTAB]$_t$ up to [CTAB]$_t = 192$ in the absence of NaBr and, in the presence of this salt, the maximum [CTAB]$_t$ and [NaBr] used were 111 and 12 mmol L$^{-1}$, respectively. For this work, the range of concentrations was limited in order to avoid a sphere-rod transition known to occur for CTAB micelles when [CTAB]$_t$ is above 200 mmol L$^{-1}$ in absence of salt. In the presence of NaBr at 100 mmol L$^{-1}$, the sphere-rod transition can occur at [CTAB]$_t$ lower than 60 mmol L$^{-1}$. 

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**Figure 1.** Conductance ($G$) versus temperature behavior of aqueous solutions of (●) SDS 400 mmol L$^{-1}$ without NaCl and (○) CTAB 137 mmol L$^{-1}$ without NaBr. The Krafft temperatures ($T_K$), showed by the arrows, are the same as those corresponding to a complete clarification of the solutions.

**Figure 2.** Conductance ($G$) versus temperature behavior of aqueous solutions of (a) (●) [SDS] = 25.32 mmol L$^{-1}$ and [NaCl] = 20 mmol L$^{-1}$; (b) (○) [CTAB] = 68.81 mmol L$^{-1}$ and [NaBr] = 22 mmol L$^{-1}$ and (●) [CTAB] = 115.45 mmol L$^{-1}$ and [NaBr] = 12 mmol L$^{-1}$. The two solutions of each surfactant have different values of $S_t$ and $C_{\text{ad}}$ but because $F(C_t)(\alpha G_t + C_{\text{ad}})$ is kept the same, they have approximately the same Krafft temperature. Pairs of samples were selected by assuming $\alpha = 0.26$ for SDS and $\alpha = 0.23$ for CTAB, the best fit values. See text.
Representative conductance versus temperature curves for SDS and CTAB in the absence of added electrolyte are presented in Figure 1. Figure 2 shows such plots in the presence of added SDS and CTAB in the absence of added electrolyte are presented.

Table 1: Krafft Temperatures of SDS

<table>
<thead>
<tr>
<th>Sample</th>
<th>[SDS]/mol L(^{-1})</th>
<th>[NaCl]/mol L(^{-1})</th>
<th>(F(C_i))</th>
<th>(F(C_i)[\alpha[SDS]]+[\text{NaCl}])</th>
<th>(T_K/°C)</th>
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</thead>
<tbody>
<tr>
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<td>1.01</td>
<td>0.007</td>
<td>14.36</td>
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<td>0.027</td>
<td>16.23</td>
</tr>
<tr>
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<tr>
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<td>16.71</td>
</tr>
<tr>
<td>23</td>
<td>0.0376</td>
<td>0.051</td>
<td>1.01</td>
<td>0.089</td>
<td>18.10</td>
</tr>
</tbody>
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\(\alpha = 0.26\) (best fit value).

Table 2: Krafft Temperatures of CTAB

<table>
<thead>
<tr>
<th>Sample</th>
<th>[CTAB]/mol L(^{-1})</th>
<th>[NaBr]/mol L(^{-1})</th>
<th>(F(C_i))</th>
<th>(F(C_i)[\alpha[CTAB]]+[\text{NaBr}])</th>
<th>(T_K/°C)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>5</td>
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<tr>
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</tr>
<tr>
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<td>1.06</td>
<td>0.038</td>
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</tr>
<tr>
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<td>0.032</td>
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<td>0</td>
<td>1.07</td>
<td>0.045</td>
<td>26.95</td>
</tr>
</tbody>
</table>

\(\alpha = 0.23\) (best fit value).

Within an uncertainty of 1–2 °C. It is clear from Figure 2a that \(T_K\) is larger in the presence of salt even though \(T_K\) for the two samples is the same. This is expected. The Krafft point increases with increasing counterion concentration because the solubility of the surfactant is reduced at a faster rate than the cmc. The two samples in Figure 2a have the same value of \(C_{ad}\) for temperatures above \(T_K\), but the salt-containing sample has a larger value of \(C_{ad}\) below \(T_K\) because of the incomplete dissolution of the surfactant.
of $\alpha$ is fixed at unity. Following the procedure outlined schematically in Figure 2 of ref 2, the value of $\alpha$ was varied by trial and error until a common curve was achieved for each surfactant. The best common curves were judged by plotting the mean squared deviation ($\chi^2$) of the data from a quadratic trial function versus $R$, as shown for SDS and CTAB in Figure 5. For SDS, the plot in Figure 5a has a minimum at $R = 0.26$ with an estimate error of $\pm 0.02$. For CTAB (Figure 4b), the minimum for $R$ was $0.23 \pm 0.03$. Uncertainties in values of $R$ based on eq 3 were recently discussed in detail in the Appendix to ref 2. Figures 3b and 4b show the common curves using these values of $R$. Figure 3 also includes $T_K$ values estimated from the solubility data of Nakayama and Shinoda\textsuperscript{16} for SDS–NaCl mixtures, which fall on the same common curve with our $T_K$ measurements, being in excellent agreement with our results.

It is clear that using a constant value of $\alpha$ to find the common curves in Figures 3b and 4b leads to a value of $R$ that is averaged over the two respective temperature ranges. Alpha values are known\textsuperscript{2,10} to vary slightly with temperature, often showing a broad, shallow minimum near room temperature. A small variation of $\alpha$ with temperature could be treated using a Taylor expansion over the entire range, or by experimentally studying a “constant $C_{\text{aq}}$” series, i.e., a series of samples prepared to yield the same value of $C_{\text{aq}}$.

The original hypothesis leading to the definition of $\alpha$ asserted that equal values of $N$ resulted from equal values of $C_{\text{aq}}$.\textsuperscript{1} Nevertheless, no knowledge of $N$ itself is needed\textsuperscript{1} to find the value of $\alpha$ either by matching pairs of samples with the same value of $C_{\text{aq}}$ or by searching for common curves such as those in Figures 3b and 4b. If, in fact, values of $N$ are available, as is the case with SDS,\textsuperscript{19} then any property that is a function of $C_{\text{aq}}$ may also be plotted as a function of $N$. Such a plot is given for values of $T_K$ in Figure 5. The abscissa in Figure 6 was computed using the consensus values of $N$ for 25 °C.

![Figure 4](image-url)  
**Figure 4.** Krafft temperature, $T_K$, versus $F(C)\{\alpha C + C_{\text{aq}}\}$ for CTAB (a) $\alpha = 1$ and (b) best fit value of $\alpha = 0.23$. Open symbols (○) are for salt free samples and filled symbols (●), for NaBr added.

![Figure 5](image-url)  
**Figure 5.** Mean square deviations, $\chi^2$, of the values of $T_K$ from a quadratic trial function for (a) SDS and (b) CTAB as a function of the degree of dissociation, $\alpha$.

![Figure 6](image-url)  
**Figure 6.** Krafft temperature, $T_K$, versus aggregation number, $N = k_2(C_{\text{aq}})^2$, for SDS. $\alpha = 0.26; \gamma = 0.25$, and $k_2 = 164.19$. Open symbols (○) are for salt free samples and filled symbols (●) are for NaCl added.
SDS are known to vary with the temperature. Averaging the results from two TRFQ studies and a SANS study, the aggregation number decreases by 0.5 ± 0.3 molecules per degree. Because, over the temperature range of Figure 6, 17.5 ± 3°C, N is predicted to vary by only 1.5 molecules, corrections have not been made to the plot. The data conform to a straight line; however, because the range of N is restricted, it is not yet clear if there is any theoretical significance in the linear behavior.

Discussion

An ionic surfactant dissolves in water up to the saturation concentration above which a hydrated solid surfactant phase separates. At temperatures below the Krafft point, the solubility is limited because of the nature of the surfactant having a long alkyl chain. At the Krafft point, micelles begin to be formed. The Krafft point is often defined as the temperature at which the solubility versus temperature curve intersects the cmc versus temperature curve. The history of the progress of the conceptual understanding of the Krafft point beginning with the initial work published in 1895 until 1988 is summarized in the paper by Moroi and Matuura. See also the important paper by Murray and Hartley.

The interesting temperature region between the Krafft point and the Krafft temperature, i.e., for temperatures T in the range Tp < T < Tk, has been a matter of debate and has led Moroi and Matuura to propose the term “micelle temperature range”. Another term, “the critical micelle temperature”, was introduced by Mazer et al. It seems to us that conductivity would be an excellent way to predict Tk from different combinations of salt and surfactant and could help in the planning of experiments that must be performed above the Krafft temperature. The same kind of relationship can also be found for the aggregation number, N, or any other micellar property that is a function of Cm. The new method to estimate α can be applied to all ionic detergents with experimentally accessible Krafft temperatures.

Conclusions

The Krafft temperatures of SDS and CTAB were shown to be functions of the concentration of counterions in the aqueous phase whatever the counterions are provided by the surfactant or both the surfactant and added salt. The estimated values of α for SDS and CTAB are in good agreement with literature values. Thus, the present results confirm that the Krafft temperature of ionic surfactants is another of the properties through which α can be defined and derived.

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References and Notes
