ARTICLES

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

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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, α. 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 α 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 α 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, α, 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 definition[1] was demonstrated for properties such as the aggregation number, N,[2] and the micelle hydration as measured by EPR.[1,2] A recent paper[3] 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 pseudophase ion exchange mass balance relationship[4−6] is given by

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

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 $F(C_t)$[6]

$$F(C_t) = \frac{1}{1 - VC_t} \qquad (2)$$

where V is the molar volume of the anhydrous surfactant in L

mol^{-1}, assuming that the density of the surfactant is approximately 1.0 g 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 α 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

$$F(C_t)\{\alpha C_t + C_{ad}\} = \text{constant} \qquad (3)$$

when either C_t or C_{ad} are varied and an adequate value of α is employed, because the value of C_f in eq 1 is the same for a given value of C_{aq}.[1] The procedure of eq 3 is valid whether α is constant or if it varies as a function of N. There is experimental[1,7] evidence that α 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, α 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] α is also found to be approximately constant. In addition, α shows only a weak dependence with the temperature.[10] Therefore, we proceed assuming that α 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

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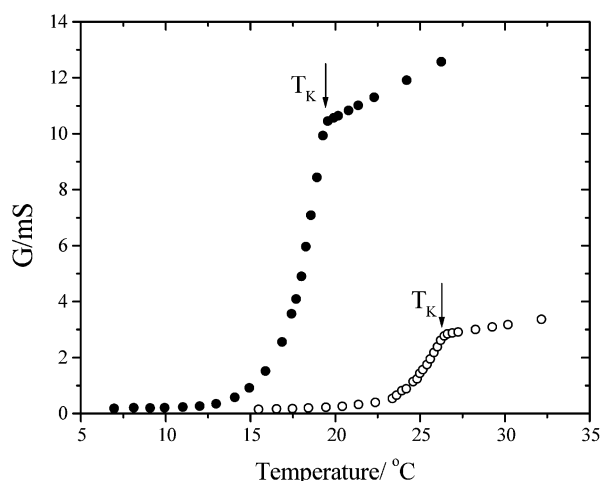
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Figure 1. Conductance (G) versus temperature behavior of aqueous solutions of (●) SDS 400 mmol L^{-1} without NaCl and (○) CTAB 137 mmol L^{-1} without NaBr. The Krafft temperatures (T_K), showed by the arrows, are the same as those corresponding to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

degree of counterion dissociation of CsDS.[3] 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_{aq}, as given by eq 1, and, second, to estimate the values of α 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 μS 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 reach a steady value. The temperature was measured using a thermocouple (precision of ± 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 ± 0.05 °C) was superior to the reproducibility in samples presumably prepared identically (averages about ± 0.1 °C). It is important to distinguish between
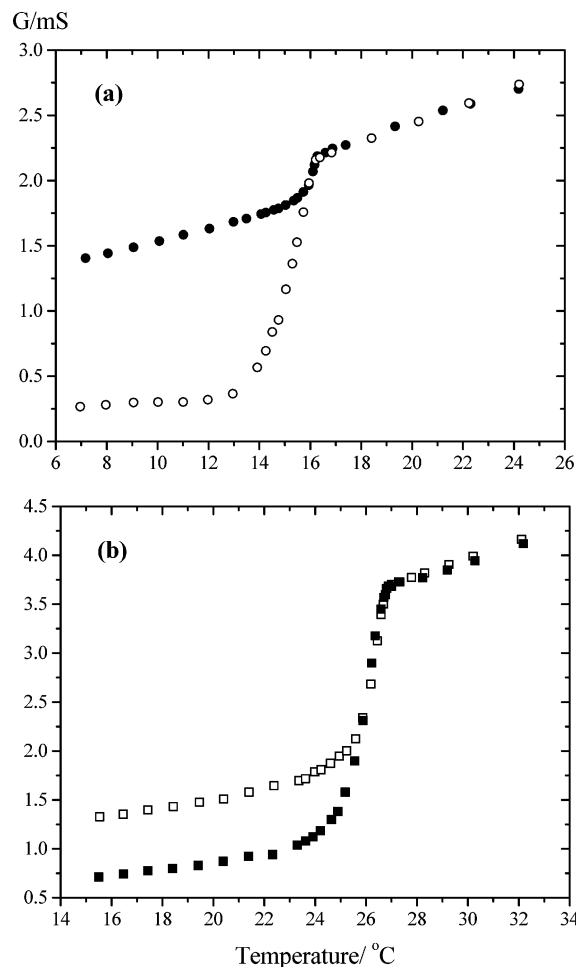

Figure 2. Conductance (G) versus temperature behavior of aqueous solutions of (a) (○) [SDS] = 100.28 mmol L^{-1} and [NaCl] = 0 and (●) [SDS] = 25.32 mmol L^{-1} and [NaCl] = 20 mmol L^{-1}; (b) (□) [CTAB] = 68.81 mmol L^{-1} and [NaBr] = 22 mmol L^{-1} and (■) [CTAB] = 115.45 mmol L^{-1} and [NaBr] = 12 mmol L^{-1}. The two solutions of each surfactant have different values of S_t and C_{ad}, but because $F(C_t)\{\alpha C_t + C_{ad}\}$ 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.

our definition of T_K and the Krafft point, T_P, which is defined[11,12] 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.[13]

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 α is constant for SDS.[1] 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.[14] 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}. [15]

TABLE 1: Krafft Temperatures of SDS

sample	[SDS]/ mol L^{-1}	[NaCl]/ mol L^{-1}	$F(C_t)^a$	$F(C_t)\{\alpha[SDS]_t+[NaCl]\}^b$	T_K/ °C
1	0.025	0	1.01	0.007	14.36
2	0.025	0.004	1.01	0.011	14.90
3	0.025	0.02	1.01	0.027	16.25
4	0.025	0.01	1.01	0.017	15.45
5	0.050	0	1.01	0.013	15.04
6	0.050	0.028	1.01	0.042	17.25
7	0.085	0	1.03	0.023	15.84
8	0.100	0	1.03	0.027	16.23
9	0.101	0.040	1.03	0.068	18.31
10	0.120	0	1.04	0.032	16.55
11	0.200	0	1.06	0.055	17.75
12	0.250	0.060	1.08	0.135	19.82
13	0.400	0	1.13	0.118	19.42
14	0.600	0	1.21	0.189	20.67
15^c	0.0917	0	1.03	0.094	15.87
16^c	0.0471	0	1.01	0.048	15.03
17^c	0.0238	0	1.01	0.024	14.21
18^c	0.0100	0	1.00	0.010	13.38
19^c	0.0653	0.005	1.02	0.072	15.87
20^c	0.0300	0.005	1.01	0.035	15.03
21^c	0.0429	0.01	1.01	0.054	15.87
22^c	0.0329	0.025	1.01	0.058	16.71
23^c	0.0376	0.05	1.01	0.089	18.10

^{a} Eq 2, using $V = 0.288$ L mol^{-1} for SDS. ^{b} $\alpha = 0.26$ (best fit value). ^{c} From the data of Nakayama and Shinoda,[16] where [SDS]$_t$ are the solubility values extracted from solubility versus temperature curves above the Krafft point (see Figure 2 of ref 16).

TABLE 2: Krafft Temperatures of CTAB

sample	[CTAB]/ mol L^{-1}	[NaBr]/ mol L^{-1}	$F(C_t)^a$	$F(C_t)\{\alpha[CTAB]_t+[NaBr]\}^b$	T_K/ °C
1	0.027	0	1.01	0.006	24.88
2	0.027	0.005	1.01	0.011	25.27
3	0.069	0	1.03	0.015	25.59
4	0.069	0.007	1.03	0.023	25.97
5	0.069	0.022	1.03	0.038	26.72
6	0.111	0.012	1.04	0.038	26.70
7	0.163	0	1.06	0.038	26.67
8	0.137	0	1.05	0.032	26.46
9	0.192	0	1.07	0.045	26.98

^{a} Eq 2, using $V = 0.364$ L mol^{-1} for CTAB. ^{b} $\alpha = 0.23$ (best fit value).

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 salt. The pairs of samples in parts a and b of Figure 2 were chosen such that they have the same value of $F(C_t)\{\alpha C_t + C_{ad}\}$ employing the best values of $\alpha = 0.26$ and 0.23 for SDS and CTAB, respectively, as detailed below. It is clear from Figure 2 that different combinations of C_t and C_{ad} giving the same value of $F(C_t)\{\alpha C_t + C_{ad}\}$ yield the same value of T_K. In the case of SDS, there is a 4-fold difference in the surfactant concentrations of the two samples (compare also samples 3 and 8 or 5 and 16 of Table 1 and samples 5, 6, and 7 of Table 2).

The plots in Figures 1 and 2 show that at low temperatures G increases slowly because the solubilities of the ionic surfactants are quite limited. During a temperature transition region, G increases sharply with increasing temperature beginning at the Krafft point, T_P, because there is an abrupt increase of the solubility of the hydrated surfactant due to micelle formation, until the Krafft temperature, as defined in previous section, is reached. Then, G increases gradually due to the increase in ionic mobility with increasing temperature. It is apparent from Figures 1 and 2 that T_K may be measured with a high degree of precision using conductivity data, whereas the Krafft point, T_P, is less well defined. Nevertheless, the value of T_P may be discerned
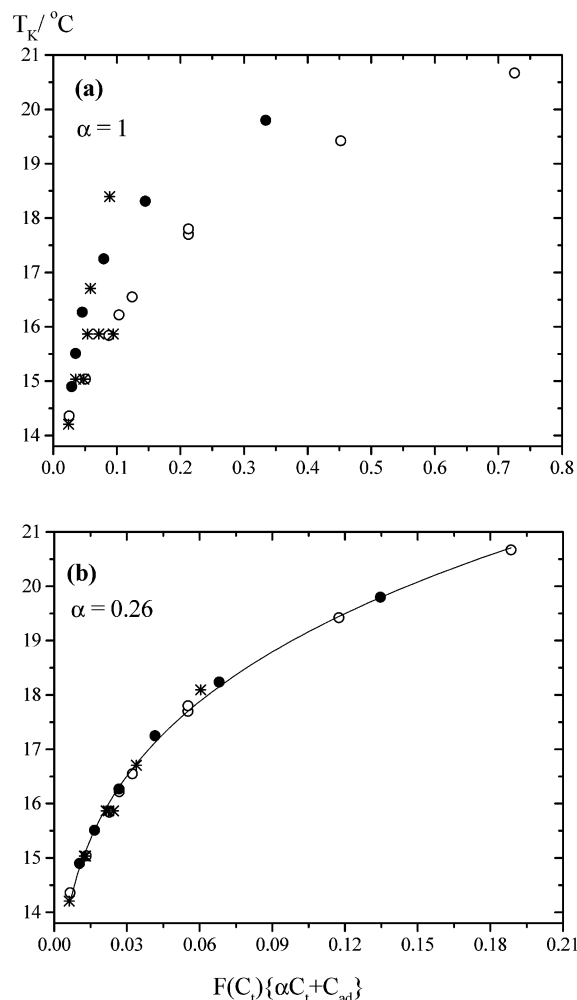

Figure 3. Krafft temperature, T_K, versus $F(C_t)\{\alpha C_t + C_{ad}\}$ for SDS (a) $\alpha = 1$ and (b) best fit value of $\alpha = 0.26$. Open symbols (○) are for salt free samples and filled symbols (●), for NaCl-added. (∗) From the solubility data of Nakayama and Shinoda.[16]

within an uncertainty of 1−2 °C. It is clear from Figure 2a that T_P 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.[12] The two samples in Figure 2a have the same value of C_{aq} for temperatures above T_K, but the salt-containing sample has a larger value of C_{aq} below T_K because of the incomplete dissolution of the surfactant.

Tables 1 and 2 collect the Krafft temperatures for SDS and CTAB, together with the calculated values of $F(C_t)$ (eq 2) and $F(C_t)\{\alpha C_t + C_{ad}\}$. The molar volumes used in eq 2 are $V = 0.288$ L mol^{-1} for SDS and $V = 0.364$ L mol^{-1} for CTAB. Table 1 also includes values of T_K for SDS deduced from the solubility measurements of Nakayama and Shinoda.[16] From Tables 1 and 2, we can see that T_K increases with an increase of C_t for $C_{ad} = 0$. If S_t is fixed, T_K increases with an increase of C_{ad} (e.g., compare samples 1, 2, 3, and 4 of Table 1 and samples 3, 4, and 5 of Table 2). This behavior is in accordance with that observed by Nakayama and Shinoda[16] and Mazer et al.[17] for SDS in aqueous NaCl solutions and by La Mesa et al.[18] for CTAB in aqueous NaBr solutions.

Figures 3 and 4 show plots of T_K as a function of $F(C_t)\{\alpha C_t + C_{ad}\}$ for SDS and CTAB, respectively, using the data extracted from Tables 1 and 2. In Figures 3a and 4a, the value
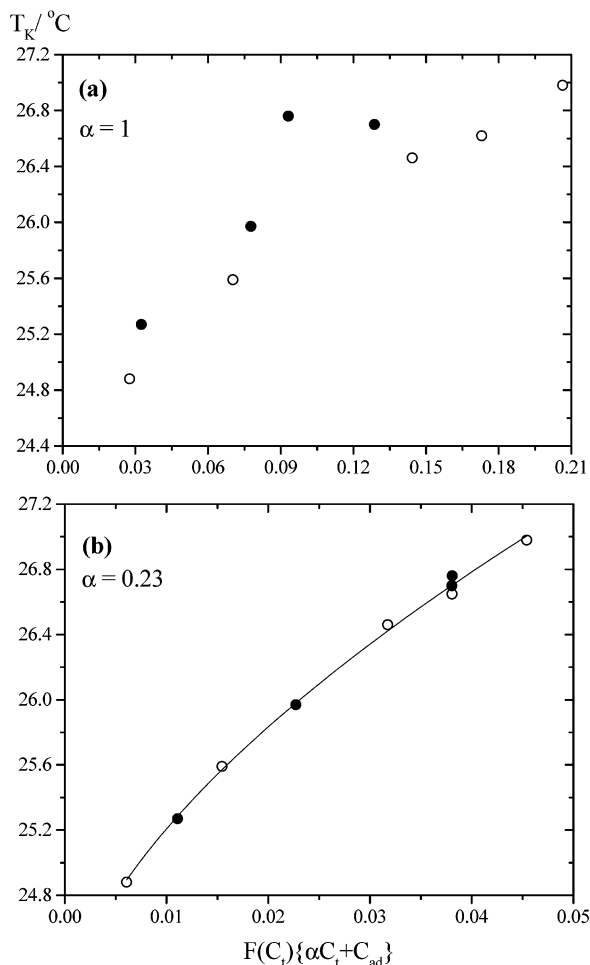
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Figure 4. Krafft temperature, T_K, versus $F(C_t)\{\alpha C_t + C_{ad}\}$ for CTAB (a) $\alpha = 1$ and (b) best fit value of $\alpha = 0.23$. Open symbols (○) are for salt free samples and filled symbols (●), for NaBr added.
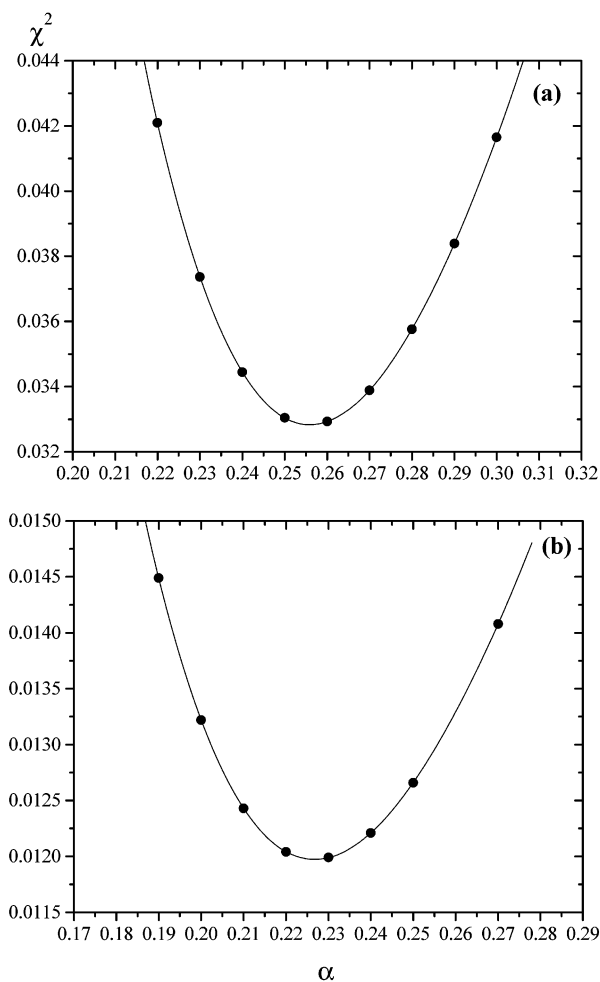

Figure 5. Mean square deviations, χ^2, of the values of T_K from a quadratic trial function for (a) SDS and (b) CTAB as a function of the degree of dissociation, α.

of α is fixed at unity. Following the procedure outlined schematically in Figure 2 of ref 2, the value of α 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 (χ^2) of the data from a quadratic trial function versus α, as shown for SDS and CTAB in Figure 5. For SDS, the plot in Figure 5a has a minimum at $\alpha = 0.26$ with an estimate error of ±0.02. For CTAB (Figure 4b), the minimum for α was 0.23 ± 0.03. Uncertainties in values of α 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 α. Figure 3 also includes T_K values estimated from the solubility data of Nakayama and Shinoda[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 α to find the common curves in Figures 3b and 4b leads to a value of α that is averaged over the two respective temperature ranges. Alpha values are known[2,10] to vary slightly with temperature, often showing a broad, shallow minimum near room temperature. A small variation of α with temperature could be treated using a Taylor expansion over the entire range, or by experimentally studying a "constant C_{aq}" series, i.e., a series of samples prepared to yield the same value of C_{aq}.

The original hypothesis leading to the definition of α asserted that equal values of N resulted from equal values of C_{aq}.[1] Nevertheless, no knowledge of N itself is needed[1] to find the value of α either by matching pairs of samples with the same
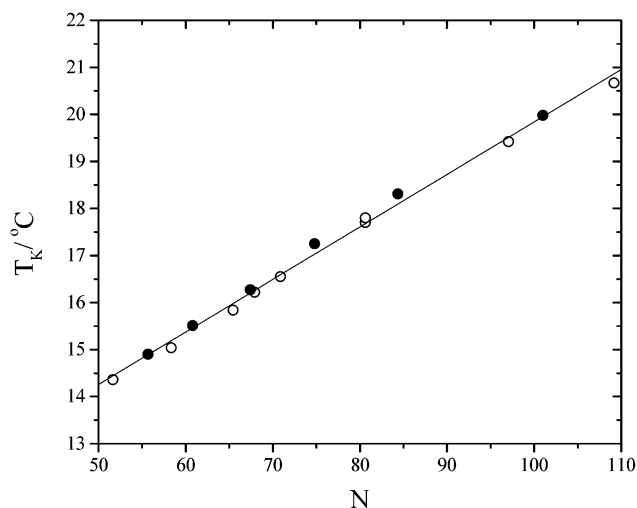

Figure 6. Krafft temperature, T_K, versus aggregation number, $N = k_2(C_{aq})^\gamma$, for SDS. $\alpha = 0.26$; $\gamma = 0.25$, and $k_2 = 164$.[19] Open symbols (○) are for salt free samples and filled symbols (●) are for NaCl added.

value of C_{aq}[1] or by searching for common curves[1] such as those in Figures 3b and 4b. If, in fact, values of N are available, as is the case with SDS,[19] then any property that is a function of C_{aq} may also be plotted as a function of N. Such a plot is given for values of T_K in Figure 6. The abscissa in Figure 6 was computed using the consensus values of N for 25 °C. Values of N for

SDS are known[20-22] to vary with the temperature. Averaging the results from two TRFQ studies[20,21] and a SANS study,[22] 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.[11] 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.[12] The Krafft point is often defined as the temperature at which the solubility versus temperature curve intersects the cmc versus temperature curve.[11] 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.[12] See also the important paper by Murray and Hartley.[13]

The interesting temperature region between the Krafft point and the Krafft temperature, i.e., for temperatures T in the range $T_P < T < T_K$, has been a matter of debate and has led Moroi[23,12] to propose the term "micelle temperature range". Another term, "the critical micelle temperature", was introduced by Mazer et al.[17] It seems to us that conductivity would be an excellent method to cast light on the debate in this intermediate temperature range, but that is beyond the scope of the present work.

Turning to the point at which $T = T_K$, the total solubility of the surfactant becomes equal to C_t. Thus, solubility data taken at any temperature $T > T_P$ may be used to evaluate T_K as a function of C_{aq}. At this temperature, C_{aq} may be computed from eq 1 by substituting the total solubility for C_t. Thus, Nakayama and Shinoda's measurements[16] of the solubility of SDS at various values of C_{ad} afford another opportunity to test our hypothesis. Taking values of the total solubility of the surfactant at temperatures $T > T_P$ for given values of C_{ad} from Figure 2 of ref 16 and computing C_{aq} from eq 1 yields the data in Table 1 which are plotted as asterisks in Figure 3.

Equation 3, as implemented for constant α, appears to work well to describe the behavior of T_K of both SDS and CTAB as a function of the surfactant and/or added salt concentration, i.e., all values of T_K fall on a common curve when plotted versus $F(C_t)\{\alpha C_t + C_{ad}\}$ if the correct value of α is employed. The value of $\alpha = 0.26 \pm 0.02$ found by T_K measurements for SDS are in good agreement with literature values based on EPR measurements ($\alpha = 0.272 \pm 0.017$, also derived by using eq 3),[1] conductivity using the Evans' method ($\alpha = 0.256$),[24] activity measurements ($\alpha = 0.27$),[25] micelle electrophoretic mobility (0.29 ± 0.01),[26] and radio isotope Na^+ mobility measurements ($\alpha = 0.27$).[27] In the case of CTAB, the obtained value of $\alpha = 0.23 \pm 0.03$ can be compared to values determined by micelle electrophoretic mobility ($\alpha = 0.24$),[28] by conductivity using the Evans' method ($\alpha = 0.22$),[28] by measurements of the rate of deprotonation of benzimidazole in CTAB−NaBr mixtures ($\alpha = 0.25$),[29] and by dynamic light scattering ($\alpha = 0.22$).[30]

The fact that two samples having the same value of C_{aq} yield the same value of T_K suggests that intermicellar interactions do not affect the precipitation of the hydrated surfactant. Because at $T = T_K$ these two samples produce micelles having the same value of N, the energetics of transferring a surfactant molecule from the hydrated solid to a micelle depends on the aggregation number, not on the concentration of micelles. It is clear that the energetics of both the hydrated solid as well as the micelle are important in determining the value of T_K.

The relationship between T_K and C_{aq}, found for both systems SDS−NaCl and CTAB−NaBr, is interesting because it offers a way to predict T_K 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 C_{aq}. 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 whethever 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.

References and Notes

(1) Bales, B. L. *J. Phys. Chem. B* **2001**, *105*, 6798.

(2) Bales, B. L.; Zana, R. *J. Phys. Chem. B* **2002**, *106*, 1926.

(3) Bales, B. L.; Benrraou, M.; Zana, R. *J. Phys. Chem. B* **2002**, *106*, 9033.

(4) Chaimovich, H.; Aleixo, F. M. V.; Cuccovia, I. M.; Zanette, D.; Quina, F. H. In *Solution Behavior of Surfactants*; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 949.

(5) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, *24*, 357.

(6) Soldi, V.; Keiper, J.; Romsted, L. S.; Cuccovia, I. M.; Chaimovich, H. *Langmuir* **2000**, *16*, 59.

(7) (a) Romsted, L. S. Rate Enhancements in Micellar Systems. Ph.D. Thesis, Indiana University, Bloomington, IN, 1975. (b) Sasaki, T.; Hattori, M.; Sasaki, J.; Nukina, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1397. (c) Stilbs, P.; Jermer, J.; Lindman, B. *J. Colloid Interface Sci.* **1977**, *60*, 232.

(8) (a) Aswal, V. K.; Goyal, P. S. *Chem. Phys. Lett.* **2002**, *357*, 491. (b) Beunen, J. A.; Ruckenstein, E. *J. Colloid Interface Sci.* **1983**, *96*, 469.

(9) (a) Stigter, D. *Prog. Colloid Polym. Sci.* **1978**, *65*, 45. (b) Gunnarsson, G.; Gustavsson, H. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2901. (c) Linse, P.; Gunnarsson, G.; Jonsson, B. *J. Phys. Chem.* **1982**, *86*, 413. (d) Evans, D. F.; Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344. (c) Jönsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley: Chichester, U.K., 1998. (f) Hayter, J. B. *Langmuir* **1992**, *8*, 2873. (g) Maeda, H. *J. Colloid Interface Sci.* **2001**, *241*, 519.

(10) Barry, B. W.; Wilson, R. *Colloid Polym. Sci.* **1978**, *256*, 251.

(11) (a) Shinoda, K. In *Colloidal Surfactants*; Academic Press: New York, 1963; Chapter I, pp 6−8. (b) Shinoda, K.; Becher, P. *Priciples of Solution and Solubility*; Marcel Dekker: New York, 1978; pp 159−162.

(12) Moroi, Y.; Matuura, R. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 333.

(13) Murray, R. C.; Hartley, G. S. *Trans. Faraday Soc.* **1935**, *31*, 183.

(14) (a) Reiss-Husson, F.; Luzzati, V. *J. Phys. Chem.* **1964**, *68*, 3504. (b) Ekwall, P.; Mandel, L.; Solyom, P. *J. Colloid Interface Sci.* **1971**, *35*, 519.

(15) Gamboa, C.; Sepulveda, L. *J. Colloid Interface Sci.* **1986**, *113*, 566.

(16) Nakayama, H.; Shinoda, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1797.

(17) Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075.

(18) La Mesa, C.; Ranieri, G. A.; Terenzi, M. *Thermochim. Acta* **1988**, *137*, 143.

(19) Quina, F. H.; Nassar, P. M.; Bonilha, J. B. S.; Bales, B. L. *J. Phys. Chem.* **1995**, *99*, 17028.

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(20) Coonen, Y.; Geladé, E.; Van der Auweraer, M.; Vandendriessche, H.; De Schryver, F. C. *J. Phys. Chem.* **1983**, *87*, 1426.

(21) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1985**, *89*, 2709.

(22) Bezzobotnov, V. Y.; Borbély, S.; Cser, L.; Faragó, B.; Gladkih, I. A.; Ostanevich, Y. M. *J. Phys. Chem.* **1988**, *92*, 5738.

(23) Moroi, Y.; Sugii, R.; Akine, C.; Matuura, R. *J. Colloid Interface Sci.* **1985**, *108*, 180.

(24) Evans, H. C. *J. Chem. Soc.* **1956**, 579.

(25) Sasaki, T.; Hattori, M.; Sasaki, J.; Nukina, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1397.

(26) Stigter, D.; Mysels, K. J. *J. Phys. Chem.* **1955**, *59*, 45.

(27) Mysels, K. J.; Dulin, C. I. *J. Colloid Sci.* **1955**, *10*, 461.

(28) Sepulveda, L.; Cortes, J. *J. Phys. Chem.* **1985**, *89*, 5322.

(29) Bunton, C. A.; Romsted, L. S.; Sepulveda, L. *J. Phys. Chem.* **1980**, *84*, 2611.

(30) Dorshow, R.; Briggs, J.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1982**, *86*, 2388.