ความไม่อิสระจากอุณหภูมิของความเข้มข้นไมเซลล์วิกฤติและความจุความร้อนของการเกิดไมเซลล์สำหรับสารลดแรงตึงผิวชนิดมีประจุ

DEPENDENCY OF CRITICAL MICELLE CONCENTRATIONS AND HEAT CAPACITIES OF MICELLE FORMATION ON TEMPERATURE FOR IONIC SURFACTANTS

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บทคัดย่อ

ความเข้มข้นไมเซลล์วิกฤติของสารลดแรงตึงผิวและการแปรเปลี่ยนค่าความจุความร้อนสำหรับการเกิดไมเซลล์เมื่อมีการแปรเปลี่ยนอุณหภูมินับเป็นสิ่งสำคัญในการหาค่าการเปลี่ยนแปลงเอนทัลปีและพลังงานที่เกี่ยวข้อง สำหรับค่าต่ำสุดของความเข้มข้นไมเซลล์วิกฤติของสารลดแรงตึงผิวประจุลบ, cmc*, ซึ่งเกิดขึ้น ณ อุณหภูมิ T^* จะพบว่าค่า cmc ณ อุณหภูมิอื่น ๆ จะขึ้นกับค่าของ cmc*, T/T^* และ $\Delta C_p/(1+\alpha)$ โดยค่า ΔC_p เป็นการแปรเปลี่ยนค่าความจุความร้อนสำหรับการเกิดไมเซลล์ และ α เป็นสัดส่วนดีกรีการเกาะตัวของประจุตรงกันข้าม ความสัมพันธ์ที่ง่าย ๆ จากการกำหนดให้ $\Delta C_p/(1+\alpha)$ มีค่าคงตัว สามารถทดสอบกับข้อมูลที่ได้จากการทดลอง 20 ชุดพบว่า มีความคลาดเคลื่อนน้อยกว่า 1% ถึง 19 ชุด และมีเพียงชุดเดียวที่มีความคลาดเคลื่อน 1.6% ซึ่งเป็นการเสนอแนะว่ากลุ่มตัวแปร $\Delta C_p/(1+\alpha)\,RT\,\ln cmc$ มีค่าเท่ากันกับค่าที่เกิดจากอันตรกิริยาระหว่างสายโซ่ไฮโดรคาร์บอน-น้ำ กับพลังงานกิบบส์ของการเกิดไมเซลล์ แต่ยังคงมีสิ่งที่คาดไม่ถึงและข้อสงสัยอีกมากมาย

ABSTRACT

The temperature dependency of the critical micelle concentration and the heat capacity changes that accompanies micelle formation is crucial in determining the enthalpy changes and associated energy. For any minimal value of critical micelle concentration of an ionic surfactant, cmc*, occurring at a temperature T^*, the cmc at other temperatures depends on cmc*, T/T^*, and $\Delta C_p/(1+\alpha)$. ΔC_p is the change in heat capacity for micellization, and α is the fractional degree of counterion binding. A simple equation, based on keeping $\Delta C_p/(1+\alpha)$ as an invariance parameter, can be used to fit 20 sets of experimental data with root mean square deviations less than 1% for 19 of them and 1.6% for the other. Hence, It can be suggested that the value of $\Delta C_p/(1+\alpha)RT \ln cmc$ is equal to the contribution of hydrocarbon chain-water interactions to the Gibbs energy of micellization, but there are several unexpected and puzzling exceptions.

INTRODUCTION

The potentialities of organized systems like micelles or microemulsions in the field of hydro-metallurgy and metal recovery, in general, have been amply discussed in the recent literature (Osseo-Asare and Zheng, 1991; Savastano and Ortiz, 1991; Stevens *et al.,* 1997; Paatero and Sjoblom, 1990; Paatero *et al.,* 1990; Vijayalakshmi, *et al.,* 1990; Vijayalakshmi and Gulari, 1991; Neuman, *et al.,* 1990). Without trying to give an exhaustive view, the following applications can be mentioned. Surface active agents are, for instance, often added in solvent extraction systems to achieve increased extraction rates (Cheng *et al.,* 2001; Osseo-Asare and Keeney, 1980). This may result in a microemulsification of the aqueous phase in the organic phase (Texter, 2001), which brings about an increase of the interfacial area. Microemulsions have been used in equilibrium with an external aqueous phase (the socalled

Winsor II systems) to concentrate metal ions to be removed from aqueous streams (Ovejero-Escudero, *et al.*, 1987) or to transport metal ions in liquid membrane processes (Tondre, and Xenakis, 1984; Derouiche and Tondre, 1990). Micellar-enhanced ultrafiltration techniques were also successfully employed for the same kind of purpose (Dunn, *et al.*, 1989; Christian, *et al.*, 1989; Klepac, *et al.*, 1991). A last example can be found in the use of microemulsions or micelles as model systems to mimic in some way the aqueous/organic interfaces found in liquid-liquid extraction (Tondre and Boumezioud, 1989; Boumezioud, *et al.*, 1989). Such model systems may help elucidating the reaction mechanisms involved and precising the locale of the complex step (Tondre and Canet, 1991).

While surfactants have not only long been important in industries as varied as cleaning and pharmaceuticals or paints and food processing, but also, over the last two decades, there has been a spurt of interest in applying surfactants to separations. The two principal motivations for this activity have been the demanding new separations required for the recovery of delicate biological molecules from fermentation broths and the increasingly demanding purifications required by the growing world-wide awareness of the need to control environmental pollution. However, the quantitative description of the mechanistic of micelle formation has yet been clear. Therefore, the objectives of this study is to determine key parameters affecting the quantitative or semi-quantitative description of the micellization process which is an obvious need for the development of the highly selective low energy processes of metal ion separation from (at least) wastewater.

THEORY

It is evident that for micelles to exist the Gibbs free energy of their formation has to be negative. Those micelles form only above the cmc indicates that there are both positive and negative contributions to the Gibbs energy, and that only above the cmc do the latter prevail. One may write $\Delta G = \Delta H - T\Delta S$ at constant temperature to separate an energy contribution ΔH from an entropic contribution ΔS. Clearly, negative values of ΔH and positive values of

ΔS favor negative values of ΔG. One expects that if the hydrophobic parts are shielded, H will decrease, as the hydrocarbon and water are incompatible whereas hydrocarbon tails amongst themselves are not. This decrease is partly offset by the fact that like ionic head groups are brought close to one another and they repel, i.e., give rise to a positive interaction energy. Noting that S is a measure of randomness, one might expect ΔS to be negative on micellization, at least as far as the amphiphiles are concerned. Thus one supposes that only when ΔH is sufficiently negative can micellization be realized.

Researchers (Ben-Naim, 1971a,b; O'Connell and Brugman, 1977) showed by simple statistical mechanical calculations using a hard sphere model that one source of the solvent effect on dimerization (and, by extension, on micellization) is that the nature of the volume available to the solvent molecules changes in such a way as to increase the entropy of the solvent. In particular, inability of the relatively small solvent molecules to penetrate the relatively large solute domains occupied either by individual solute molecules or by micelles reduces the entropy of solvent molecules near the surfaces of these domains. The total entropy decrease of the solvent is approximately proportional to the overall area of the solute domains. Since formation of micelles decreases this overall area, entropic effects of this type favor micellization. They are also greater for solvents having smaller molecules, a prediction consistent with the observed large magnitude of hydrophobic interactions in water. Thus, entropy changes for both the surfactant and water must be considered in calculating ΔG^o for micellization.

Thermodynamics of micellization

Critical micelle concentrations (cmc) have been determined as a function of temperature for many ionic surfactants. Such results often define a U-shaped curve with a minimum not far from room temperature (Kresheck, 1975). These have been used to evaluate changes in thermodynamic properties for micellization. For micelles that consist of m surfactant ions and p counterions, with $\alpha = p/m$, the usual procedure is to write

$$\Delta G_m^o = (1+\alpha) RT \ \ln cmc \tag{1}$$

$$\Delta H_m^o = (1+\alpha) RT^2 \ d(\ln cmc)/dT \tag{2}$$

under conditions of constant pressure. Attempts to obtain the corresponding heat capacity changes, ΔC_p, from the temperature derivatives of ΔH_m^o have met with limited success, because the result at any particular temperature is very sensitive to possible small errors in the nearest data points. It sometimes appears that ΔC_p varies with the temperature rather erratically (Adderson and Taylor, 1964; Stead and Taylor, 1969; Adderson and Taylor, 1970; Adderson and Taylor, 1971).

A decade ago some of these observations were reexamined by La Mesa, who introduced a very interesting "reduced variables" treatment (La Mesa, 1990). When cmc^* is the minimal value of cmc and T^* the temperature at the minimum, he found that plotting $(cmc - cmc^*)/cmc^*$ against $|(T-T^*)/T^*|$ for an assortment of surfactants gave points falling fairly close to a single curve represented by the empirical equation

$$(cmc - cmc^*)/cmc^* = |(T-T^*)/T^*|^\gamma \tag{3}$$

with $\gamma = 1.74 \pm 0.03$. The exponent γ has no obvious physical meaning, and it is not clear why Eq. 3 works as well as it does or what is the main source of the deviations of data points from the curve.

These considerations suggested taking a further look at these U-shaped curves to find whether a relation similar to Eq. 3 can be derived thermodynamically. The results, presented here, appear to offer a more satisfying way to analyze this sort of data, especially when the goal is to find ΔC_p.

There has been much discussion regarding the applicability of Eq. 3, in light of the fact that the aggregation number, m, and the number of bound counterions, p, are not expected to be independent of the temperature (Kresheck, 1975; Muller, 1977). For ionic surfactants, it is reassuring that good agreement is found when results from Eq. 2 can be compared with those from calorimetric measurements (Kresheck, 1975; Muller, 1977; Bach *et al.*, 1995). In this study, the validity of Eq. 2 is provisionally assumed in order to explore more fully what it implies about the variation of cmc with temperature in the neighborhood of the minimum.

When the temperature range is not too wide, a reasonable first approximation is to treat ΔC_p as a constant. Noting that Eq. 2 implies that ΔH_m^o vanishes at T^*, it follows that at other temperatures

$$\Delta H_m^o = \Delta C_p \left(T - T^* \right) \tag{4}$$

while $\quad \Delta S_m^o = \Delta S_m^{o*} + \Delta C_p \ln \left(T/T^* \right) \tag{5}$

where ΔS_m^{o*} is the entropy change at T^* and is equal to $-\Delta G_m^{o*}/T^*$. Then

$$\Delta G_m^o = \Delta C_p \left[\left(T - T^* \right) - T \ln \left(T/T^* \right) \right] - T \Delta S_m^{o*} \tag{6}$$

and by Eq. 1

$$\ln cmc = \left[\Delta C_p / (1+\alpha) R \right] \left[\left(T - T^* \right)/T \, + \, \ln \left(T^*/T \right) \right] \, - \, \Delta S_m^{o*} / (1+\alpha) R \tag{7}$$

Since when $T = T^*$

$$\ln cmc^* = - \, \Delta S_m^{o*} / (1+\alpha) R \tag{8}$$

this gives $\quad \ln \left(cmc/cmc^* \right) = \left[\Delta C_p / (1+\alpha) R \right] \left[1 \, - \, T^*/T + \, \ln \left(T^*/T \right) \right] \tag{9}$

or $\quad cmc = cmc^* \exp \left[\Delta C_p \, F \left(T, T^* \right) / (1+\alpha) R \right] \tag{10}$

where $F \left(T, T^* \right)$ is an abbreviation for the function $\left[1 \, - \, T^*/T + \, \ln \left(T^*/T \right) \right]$. Eqs. 9 and 10 are indeed reduced variables equations in that the ratio cmc/cmc^* depends only on T/T^* if ΔC_p and α are fixed. They differ from Eq. 3 because each surfactant is allowed to have its own characteristic value of $\Delta C_p / (1+\alpha)$. Moreover, the function $F \left(T, T^* \right)$, like the experimental curves, is not symmetrical about the point $T = T^*$. It is significant that Eq. 9 shows that the shape of each curve is almost exclusively determined by the value of ΔC_p. This was noted earlier in papers where equations somewhat akin to Eq. 9 were also presented (Musbally, *et al.*, 1974; Musbally, *et al.*, 1976), but these relate $cmc(T)$ to the values of cmc, ΔH_m^o, and ΔC_p at 25 °C rather than to cmc^*, T^*, and ΔC_p.

A possible way to obtain an expression superior to eq 9 is to remove the assumption that ΔC_p is constant, replacing it by the slightly more realistic but still simple assumption of a linear dependence, or

$$\Delta C_p = \Delta C_p^* \left[1 - B \left(T - T^* \right) \right] \tag{11}$$

where B is a constant which needs to be determined empirically and is probably no larger than 0.01 (Musbally, *et al.*, 1976). Then using the reasoning described above, it is easily shown that

$$\ln\left(cmc/cmc^*\right) = \left[\Delta C_p^* / (1 + \alpha) R\right] \left[F\left(T, T^*\right) - BF_1\left(T, T^*\right)\right] \qquad (12)$$

where $F_1\left(T, T^*\right)$ stands for the function $\left[T^* \ln\left(T/T^*\right) + \left(T^{*2} - T^2\right)/2T\right]$. Unlike $F\left(T, T^*\right)$, which is negative whenever $T \neq T^*$, the function $F_1\left(T, T^*\right)$, is positive when $T < T^*$ and negative when $T > T^*$.

Closely similar reasoning has been used to derive equations analogous to Eqs. 6 and 12 which describe the temperature dependence of the Gibbs energy of denaturation for a single domain globular protein assumed to undergo two-state unfolding (Becktel and Schellman, 1987; Franks, *et al.*, 1988).

RESULTS

To provide a suitable test of the usefulness of Eq. 9 or 12, a data set should consist of no fewer than about 10 points covering a moderately large temperature range and preferably presented in numerical rather than graphical form. Twenty such data sets were used and are described in Table 1. Eleven of these represent a variety of cationic surfactants and the other nine pertain to seven linear and branched sodium alkylsulfates (Mukerjee and Mysels, 1971). For sodium decyl and sodium dodecyl sulfate, two data sets of similar quality were found and used separately to test the consistency of the results.

According to Eq. 9, $\ln cmc$ is linearly dependent on $F\left(T, T^*\right)$, the intercept being $\ln cmc^*$ and the slope $\Delta C_p / (1 + \alpha) R$. Therefore, each set of data was treated in the following way: with a fixed trial value of T^*, $F\left(T, T^*\right)$ was evaluated for each data point, and a plot of $\ln cmc$ versus $F\left(T, T^*\right)$ was prepared. If the plot showed appreciable curvature, a new trial value of T^* was chosen and the procedure repeated until the curvature was reduced as much as possible. The slope and intercept of the most nearly linear plot were used to obtain cmc^* and $\Delta C_p / (1 + \alpha)$, and then a calculated cmc was obtained at each temperature by means of Eq. 10.

The parameters found for each of the surfactants, and the root mean square (rms) values of the percent differences between the observed and calculated *cmc*'s, are also presented in Table 2.

It is evident that Eq. 9 fits the data surprisingly well. The only set which has rms deviation larger than 0.85% is the first; there the three largest deviations are 2.05, 2.09, and 3.09%, and the rms deviation is 1.55%. As it happens, this system is the only one for which error limits are explicitly given in the original papers (Adderson and Taylor, 1964; Stead and Taylor, 1969; Adderson and Taylor, 1970; Adderson and Taylor, 1971); they are said to be ± 0.2 mm, which amounts to just under 2%. Thus, the discrepancies between calculated and observed values are probably within the error limits in this case, and almost certainly so for the other surfactants.

Table 1 Data sets used to test Eqs. 9 and 12 (Mukerjee and Mysels, 1971).

Data set	Compounds	temp. range ($^{\circ}$C)	no. of points
1	dodecyl pyridinium bromide	5-70	14
2	1-dodecyl-4-methoxypyridinium bromide	5-55	11
3	l-dodecyl-4-methoxypyridinium chloride	5-60	12
4	l-methyl-4-dodecyloxypyridinium bromide	15-60	10
5	l-tetradecyl-4-methoxypyridinium bromide	20-60	9
6	decyl α-picolinium bromide	5-70	14
7	dodecyl α-picoliniun bromide	10-70	12
8	tetradecyl α-picolinium bromide	10-70	13
9	decyltrimethylammonium bromide	5-70	14
10	Dodecyltrimethylammonium bromide	5-70	14
11	Dodecylbenzyldimethylammonium bromide	10-70	13
12	sodium n-octyl sulfate	10-55	10
13	sodium n-decyl sulfate	0-65	14
14	sodium n-decyl sulfate	10-55	10
15	sodium 2-decyl sulfate	10-65	12
16	sodium n-dodecyl sulfate	0-65	14
17	sodium n-dodecyl sulfate	10-55	10
18	sodium n-tetradecyl sulfate	25-75	11
19	sodium 2-tetradecyl sulfate	10-65	12
20	sodium 4-tetradecyl sulfate	25-75	11

Table 2. Numerical result of data sets used to test Eqs. 9 and 12.

data set	Compounds	10^5 cmc* (mole fraction)	T*(°C)	$\dfrac{-\Delta C_p}{(1+\alpha)}$	rms dev. (%)
1	dodecyl pyridinium bromide	20.14	13	241	1.55
2	1-dodecy1-4-methoxypyridinium bromide	15.14	17	323	0.41
3	l-dodecyl-4-methoxypyridinium chloride	22.05	28.6	219	0.5
4	l-methyl-4-dodecyloxypyridinium bromide	6.13	12	291	0.4
5	l-tetradecyl-4-methoxypyridinium bromide	3.56	4	256	0.84
6	decyl -picolinium bromide	83.23	23	236	0.75
7	dodecyl -picoliniun bromide	18.35	19	267	0.69
8	tetradecyl -picolinium bromide	4.6	13	332	0.72
9	decyltrimethylammonium bromide	113	25	168	0.7
10	dodecyltrimethylammonium bromide	26.4	20	241	0.39
11	Dodecylbenzyldimethylammonium	9.86	18	328	0.77
12	sodium n-octyl sulfate	238	28.5	272	0.78
13	sodium n-decyl sulfate	58.7	30	253	0.24
14	sodium n-decyl sulfate	59.6	27	291	0.40
15	sodium 2-decyl sulfate	80.5	38	259	0.43
16	sodium n-dodecyl sulfate	14.8	25	308	0.42
17	sodium n-dodecyl sulfate	15.1	24	308	0.52
18	sodium n-tetradecyl sulfate	3.67	20	325	0.25
19	sodium 2-tetradecyl sulfate	5.89	27	333	0.26
20	sodium 4-tetradecyl sulfate	9.09	32.5	350	0.23

A consequence of the excellent fits obtained with Eq. 9 is that it is not possible to do significantly better by using Eq. 12. The data do not prove that ΔC_p is constant, but they do not allow meaningful nonzero values of the parameter B in Eq. 12 to be evaluated. Similarly, these results can not be said to prove the correctness of Eq. 2, but by themselves they give no

indication that it is incorrect. The procedure presented here probably provides the best values of $\Delta C_p/(1+\alpha)$ that can be obtained from this sort of measurement. Its main strength is that each value is determined collectively by the whole set of data and hence much less sensitive to possible errors in a few points.

The uncertainty of the final values of $\Delta C_p/(1+\alpha)$ is difficult to specify precisely and depends on which set of data is taken. When the rms deviation is relatively large, or when T^* lies outside the range spanned by the experimental points, it is found that T^* may be changed by 1, 2, or possibly even 3 °C, with concomitant changes of up to about 10% in the slopes of the plots, without making the fit very much worse. This suggests uncertainty limits of about +10%, or somewhat less when the rms deviation is small. In this connection, it may be noted that data sets 13 and 14 give two values of $\Delta C_p/(1+\alpha)$ for sodium n-decyl sulfate, each differing from their average by 7%. There is no obvious reason to expect one set of results to be better than the other. Sets 16 and 17, for sodium n-dodecyl sulfate, each give the same value of $\Delta C_p/(1+\alpha)$.

DISCUSSION

Heat capacities of micellization

The results in Table 2 provide a partial explanation for the degree of success of La Mesa's treatment (La mesa, 1990), which gave Eq. 3. The new Eq. 9 would itself define a "universal" curve if $\Delta C_p/(1+\alpha)$ were the same for all the surfactants, and with only two exceptions the actual values differ from a mean of -275 J/(mol K) by no more than about 20%. It seems likely that those surfactants considered by La Mesa that were not included here have similar heat capacities of micellization.

Like all previous treatments of these data, the present one provides unambiguous thermodynamic quantities only if the degree of counterion binding, α, is known. This quantity itself depends somewhat on temperature and rather more on the nature of the surfactant

headgroup, the length of the alkyl chain, and the counterion (Kresheck, 1975). Values of α at 25 °C were found in the literature for about half of the surfactants considered here, and these were used as a guide for estimating the missing ones. All are listed, together with the resulting values of ΔC_p, in the first two columns of Table 3. For materials having a given chain length, the experimental values typically fall in a rather narrow range, and therefore it seems unlikely that any of the estimated values will be in error by more than 0.05, leading to uncertainties not exceeding 3% in $1+\alpha$.

Calorimetric results for comparison are available for only six of the surfactants. For dodecylpyridinium bromide, data set 1, a thermometric titration method (Kresheck and Hargraves, 1974) gave -385 ± 20 J/(mol K), about 10% smaller than the value obtained here. For decyltrimethylammonium bromide, data set 9, two treatments of the same data (Musbally, *et al.*, 1974 and 1976) gave -302 $\pm$20 and -365 J/(mol K); the smaller value is very near that in Table 3. For dodecyltrimethylammonium bromide (Bach *et al.*, 1995), data set 10, calorimetric measurements at three temperatures yield -423 $\pm$20J/(mol K), in good agreement with the present value. Each of the sodium alkyl sulfates has been studied several times (Musbally, *et al.*, 1974 and 1976; Kresheck and Hargraves, 1974; Opatowski, *et. al.*, 2002). Values reported for the octyl sulfate, data set 12, are -280 $\pm$30 (Musbally, *et al.*, 1974), -325 (Musbally, *et al.*, 1976), and -310 $\pm$38 (Kresheck and Hargraves, 1974) J/(mol K), all considerably smaller than the present results. For the decyl sulfate, data sets 13 and 14, they are -394 $\pm$10 (Musbally, *et al.*, 1974), –425 (Musbally, *et al.*, 1976), and -402 $\pm$42 (Kresheck and Hargraves, 1974) J/(mol K), close to the lesser of the two values in Table 3. For the dodecyl sulfate, data sets 16 and 17, they are -516 $\pm$10 (Musbally, *et al.*, 1974), -530 (Musbally, *et al.*, 1976), -561 $\pm$42 (Kresheck and Hargraves, 1974), and -573 $\pm$20 J/(mol K), and the value found here from both sets of data is very close to the average of these.

Table 3. Thermodynamic parameters for micellization at 25 $^\circ$C of surfactants listed in Table 2.

data set	$1+\alpha$	$-\Delta C_p$ (J/(mol K))	$-\Delta G_m^o$ (kJ/mol)	ΔH_m^o (kJ/mol)	ΔS_m^o (J/(mol K))	$\dfrac{-\Delta S_m^o}{\Delta C_p}$
1	1.77[a]	427	37.3	-5.2	107.7	0.252
2	1.78[b]	575	38.8	-4.6	114.5	0.199
3	1.78[b]	390	37.2	1.4	129.3	0.332
4	1.78[b]	518	42.6	-6.7	120.3	0.232
5	1.83[b]	468	46.1	-9.9	121.6	0.260
6	1.70[c]	401	29.9	-0.8	97.5	0.243
7	1.78[c]	475	37.9	-2.9	117.7	0.248
8	1.80[c]	598	44.5	-7.2	124.9	0.209
9	1.72[d]	289	29	0.0	97.0	0.336
10	1.82[d]	439	37.2	-2.2	117.3	0.267
11	1.78[d]	584	40.7	-4.1	122.6	0.210
12	1.64[b]	446	24.6	1.6	87.6	0.196
13	1.70[a]	430	31.3	2.1	112.3	0.261
14	1.70[a]	495	31.3	1.0	108.3	0.219
15	1.70[b]	440	29.9	5.7	119.5	0.272
16	1.78[a]	548	38.9	0.0	130.5	0.238
17	1.78[a]	548	38.8	-0.6	128.3	0.234
18	1.87[a]	608	47.3	-3.0	148.5	0.244
19	1.87[b]	623	45.1	1.2	155.6	0.250
20	1.87[b]	655	43.1	4.9	170.0	0.246

a. from reference (Kresheck, 1975).   b. estimate from this study.

c. from reference (Adderson and Taylor, 1970).   d. from reference (Adderson and Taylor, 1971).

Thermodynamics of micellization

The quantities ΔG_m^o, ΔH_m^o, and ΔS_m^o have previously been calculated for most of these surfactants using Eqs. 1 and 2. It is now possible instead to use Eqs. 1, 4, 5 and 8. The results at 25 °C, also presented in Table 3, are based on *cmc*'s converted to mole fraction units, to provide unitary entropy and Gibbs energy changes. They are quite similar to values reported earlier (Adderson and Taylor, 1964; Stead and Taylor, 1969; Adderson and Taylor, 1970; Adderson and Taylor, 1971), except for differences arising because the earlier researchers used Eqs. 1 and 2 either with the assumption $\alpha = 0$ or with $\alpha = 1$. Moreover, quantities calculated at other temperature by the present approach vary with the temperature smoothly and regularly, which was not always found before. This reflects the fact that each value now depends on parameters adjusted to fit the whole data set and hence is much less severely affected by a few possible defective data points.

Table 3 also includes values at 25 °C for the ratio $\Delta S_m^o / \Delta C_p$, which is discussed below. This quantity is independent of the value adopted for α.

A number of researchers (Kumar *et al.*, 1997; Emerson and Holtzer, 1967; Evans and Ninham, 1983) have reported attempts to separate changes in thermodynamic variables for micellization into additive contributions representing, on the one hand, interactions between hydrocarbon chains and water (subscript hc) and, on the other, headgroup, counterion, and surface interactions (subscripts). The treatment of Evans and Ninham (1983) suggests that the Gibbs energy change given by Eq. 1 should be identified with the alkyl chain contribution, ΔG_{hc}^o, and that $\Delta G_s^o = -\alpha RT \ln cmc$, so that $RT \ln cmc = \Delta G_{hc}^o + \Delta G_s^o$. It would then be consistent to suppose that the changes in enthalpy and entropy given by Eqs. 2 and 4, as well as the corresponding heat capacity changes, should also be determined mainly by hydrocarbon chain-water interactions. In the following paragraphs, it will be shown that the data, broadly speaking, support this interpretation. However, a number of discordant results that cannot readily be rationalized on this basis are listed at the end of the discussion.

The hydrocarbon chain terms should show significant similarities to the changes of thermodynamic variables for the transfer of alkanes or alkyl groups from water into nonpolar solvents (Kumar *et al.*, 1997). Such transfers have the following characteristics: (1) $\Delta C_{p,tr}$ is negative and proportional to the surface area of the hydrocarbon molecule or group (Gill, *et al.*, 1985). (2) The unitary entropy change, ΔS_{tr}^o is positive, and at 25 °C the ratio $\Delta S_{tr}^o / \Delta C_{p,tr}$ is approximately –0.26 (Sturtevant, 1977; Baldwin, 1986; Muller, 1990). (3) ΔH_{tr}^o is positive at low temperatures, passing through zero near 22 °C and becoming negative on further heating (Baldwin, 1986). It may then be expected that the data in Table 3 should show similar characteristics, and to a large extent they do so.

Looking first at the heat capacity changes, they are indeed invariably negative. The table includes several pairs or groups of surfactants belonging to the same homologous series. For most of these (but not those in data sets 2 and 5), the magnitude of ΔC_p increases with increasing length of the alkyl chain, by an average of about 50 J/(mol K) per added methylene group. Data for the transfer of pentane and hexane from water solution to the pure liquid state (Gill, *et al.*, 1976) or for transfer of various hydrocarbon gases from aqueous solution to vapor (Dec and Gill, 1985) give increments of 50 ±10 J/(mol K) per added methylene group, a very satisfactory agreement.

Turning to the ratio $\Delta S_m^o / \Delta C_p$, the average of the values in Table 3 is –0.247, quite near the Sturtevant value (Sturtevant, 1977), and 12 of the 18 surfactants give values that differ from the average by 10% or less. Sturtevant's discussion suggests that this would not be expected if the entropy and heat capacity changes included major contributions not attributable to hydrophobic hydration.

Finally, transfer enthalpies of six hydrocarbons from aqueous solution to the liquid state are zero at an average temperature of 22 °C, but with some variation from compound to compound (Baldwin, 1986). For the surfactants, $\Delta H_m^o = 0$ at T^*, and according to Table 2 the average value of T^* is also 22 °C. None of the values deviate by more than ±18 °C, which corresponds to ±6% when Kelvin temperatures are used. The micellization enthalpies at 25 °C

in Table 4.5 are always much smaller than the Gibbs energy changes and seldom much larger than values of ΔH_{tr}^o reported for hydrocarbon liquids (Baldwin, 1986).

These considerations provide considerable support for the hypothesis that the changes in thermodynamic variables appearing in Table 3 arise almost exclusively from interactions of the hydrocarbon chains with water. However, a number of difficulties remain which suggest that this view cannot be entirely correct.

For the homologous compounds in data sets 2 and 5, adding two methylene groups to the chain decreases by 107 J/(mol K), where an increase of about this magnitude would have been expected.

Surfactants in data sets 2 and 3 have the same cation with different counterions, and $\left|\Delta C_p\right|$ is 185 J/(mol K) smaller for the chloride than the bromide. For the dodecylpyridinium salts, it was reported that $\left|\Delta C_p\right|$ is 100 J/(mol K) larger for the chloride than for the bromide (Kresheck and Hargraves, 1974). Since the degree of counterion binding should depend only slightly on the nature of the ion (Kresheck, 1975), neither finding is easy to rationalize.

Four of the surfactants give values of $\Delta S_m^o/\Delta C_p$ near -0.20, and two others give values near -0.33, rather far from the expected -0.26. None of these is otherwise abnormal in any obvious way, which makes it hard to suggest an explanation for these deviations.

Finally, when compared with the hydrocarbon transfer data, most of the heat capacities of micellization are unexpectedly small. For example, $\Delta C_{p,tr}$ for hexane is -440 J/(mol K) (Gill, *et al.*, 1976), and the corresponding entries in Table 3 for surfactants in data sets 1 and 10, each with a dodecyl chain, are both smaller than this. It is possible, of course, that micellization removes only a portion, rather than the entire hydrocarbon chain, from contact with water (Kumar *et al.*, 1997).

Since the materials considered here have a great variety of headgroups, it is hardly surprising that some of them show deviant behavior. However, it should be noted that almost every family of surfactants represented in the tables includes at least one member that behaves "normally". Thus, it is impossible to identify any molecular characteristic that leads to an anomalous heat capacity of micellization.

Apart from the present results, there are aspects of Evans and Ninham's treatment (Evans and Ninham, 1983) that are puzzling. For example, it requires that, for each material, in the absence of added electrolyte, $\Delta G^o_{hc}/\Delta G^o_s = -(1+\alpha)/\alpha$, and the degree of counterion binding is so nearly the same for different surfactants that this ratio can probably vary only within the rather narrow range -2.27 $\pm$ 0.15. Moreover, there is no reason why this equality should be required only at 25 °C, and if it is to hold over an extended range of temperatures, then it is also necessary to have both $\Delta S^o_{hc}/\Delta S^o_s$ and $\Delta H^o_{hc}/\Delta H^o_s$ equal to $-(1+\alpha)/\alpha$. (Strictly speaking, one should allow for the fact that a decreases on heating, but $d\alpha/dT$ is so small that this has little effect.) It is hard to see why all this should be expected for diverse ionic surfactants irrespective of chain length, headgroup structure, or counterion. It is particularly puzzling that these conditions would imply that at temperatures close to T^* both ΔG^o_{hc} and ΔG^o_s must be almost entirely of entropic origin. This has of course long been recognized for ΔG^o_{hc}, but no reason has been proposed for believing that it should be true also for ΔG^o_s.

A possible alternative conjecture that fits the present results about equally well is that $\Delta \bar{G}^o_{hc} \cong \Delta G^o_m = (1+\alpha)RT \ln cmc$ and $\Delta G^o_s \cong 0$, when there is no added electrolyte. One hesitates to propose this because it would require rejecting the model calculations used by Evans and Ninham to evaluate ΔG^o_s, but it should be noted that ΔG^o_s includes opposing terms representing attractive and repulsive interactions that allows at least the possibility of nearly complete cancellation, and the researchers themselves describe these terms as "extraordinarily difficult to quantify" (Evans and Ninham, 1983). Small nonzero values of ΔG^o_s arising from slightly unequal opposing terms might then partially account for the small and irregularly varying values of ΔH^o_m at 25 °C reported in Table 3.

CONCLUSION

From the numerical study, with the assumption that $\Delta C_p/(1+\alpha)$ is temperature independent, an equation is derived showing that the *cmc* at any temperature is a function of this quantity, cmc^*, and T/T^*. For 20 sets of data taken from the literature, it fits 19 with rms

deviations less than 1% and the other with a 1.6% deviation. An alternative equation is also presented, assuming that ΔC_p is a linear function of T, but it does not provide appreciably better fits. Although this treatment does not prove that $\Delta C_p/(1+\alpha)$ is actually constant, it gives a value for each surfactant that is consistent with all points in the data set, relatively little affected by the possible presence of a few deviant points, and hence probably the best that can be obtained from temperature-dependent *cmc* measurements. Using experimental or estimated values of $(1+\alpha)$, the data yield micellization heat capacities in fairly good agreement with the rather few available calorimetric results.

The calculated values of ΔC_p make it possible to test the suggestion (Evans and Ninham, 1983) that the quantity $(1+\alpha)RT \ln cmc$, often taken as the total Gibbs energy of micellization, is actually to be regarded as the hydrocarbon chain contribution to this Gibbs energy. Many of them are consistent with this hypothesis, but there are some unexpected and puzzling exceptions. Although the estimated uncertainties of the heat capacity changes may be as large as 10%, these discrepancies seem too large to be attributed to experimental errors.

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