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ORIGINAL CONTRIBUTION

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Enthalpy-entropy compensation in ionic micelle formation

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Abstract The enthalpy-entropy compensation in ionic surfactant micellization process over a large temperature range is examined. The surfactants SDS and $C_{16}TAB$ are investigated experimentally, and the enthalpy and entropy changes are evaluated based on phase separation or mass action models together with the other three surfactant systems. The relationship between compensation temperature and the reference temperatures is discussed.

Key words Enthalpy-entropy compensation – ionic surfactant – critical micelle concentration – reference temperature – temperature effect

Introduction

Hydrophobicity plays an important role in the thermodynamics of surfactant micellization [1, 2]. The ionic surfactants appear to almost universally possess a minimum in CMC versus temperature plot [3], which is similar to the solubility curve of the hydrophobic substance. The concept of "iceberg" by Franks and Evans [4] has been applied to micelle formation [5].

Recently, based on experiments over a wide range of temperature, many workers have re-examined the nature of the hydrophobic effect (e.g., [6–10]). Experimental evidences against the existence of a highly structured water layer (the iceberg) were accumulated and discussed in ref. [7]. It was shown that the enthalpy and entropy changes for hydrophobic substance dissolution and protein unfolding process was actually a compensation process which gives a near constant Gibbs free energy change [11, 12]. The two reference temperatures, T^* ($= 112\,^\circ\mathrm{C}$) and T_H, at which the entropy and enthalpy change for each hydrophobic compound in a series were respectively a common value, were found to be essential in hydrophobicity [13, 14].

In micellization process, the ΔH versus ΔS plot (the compensation plot) usually exhibits a linear character and the slope has a dimension of temperature and is referred to as the compensation temperature T_c [15–17]. The compensation temperature is proposed as a characteristic of solute-solute and solute-solvent interactions [18, 19].

It is the purpose of the present report to examine the enthalpy-entropy compensation in ionic surfactant micellization process over a large temperature range. The surfactants SDS and $C_{16}TAB$ are investigated experimentally, and the enthalpy and entropy changes are evaluated together with the other three surfactant systems. The relationship between compensation temperature and reference temperatures is discussed.

Experimental

SDS and $C_{16}TAB$ were all of GR grade (Merck Taiwan Ltd.) and were used without further purification. Conductometric measurements were made with a Suntax Model SC-17A conductivity meter. To prevent any pressure effect, the testing vessel was vented to atmosphere through a glass condenser. Conductance measurements were made

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over the temperature range of 10° to 90 °C. The upper limit is above most SDS of $C_{16}TAB$ works in literature.

The CMC values were determined by least-square fitting the data above and below the transition point with correlation coefficient greater than 0.9999. At least three runs were conducted for each condition to check the reproducibility. The ratio of the slopes above and below the CMC was defined as the degree of dissociation β [20]. The errors in CMC and β measurements were estimated within 4% and 2%, respectively.

The thermodynamic property changes of micellization were usually evaluated based on the phase-separation (PS) or mass-action (MA) model [21]. For the PS model, the Gibbs free energy change was:

$$\Delta G = \gamma RT \ln(\mathrm{CMC}) \,, \tag{1}$$

where $\gamma = 1$ when the counterions were ionized completely, or $= 2$ when all counterions were binding to the micelle. For the MA model, the Gibbs free energy change was:

$$\Delta G = (2 - \beta) RT \ln(\mathrm{CMC}) \,. \tag{2}$$

Though they have been criticized by several investigators [22, 23], these models were used in this work.

With the Gibbs free energy change, the enthalpy and entropy change of micellization could be subsequently obtained. The values based on Eq. (1) with $\gamma = 1$ or 2, or Eq. (2) were indexed as $P1$, $P2$, or M, respectively.

Results and discussion

The CMC and β data for SDS and $C_{16}TAB$ are listed in Table 1, and are close to those reported in literature. A minimum exists in each CMC-T curve and the corresponding temperature (T_0) and CMC (CMC_0) (and also the other three surfactant systems whose CMC and β's had been studied over a wide temperature range) are evaluated via procedures proposed by LaMesa [3] and are listed in Table 2. β increases with temperature, indicating the association between the head group and the counterion is a high-temperature unfavorable process.

Table 1 Experimental results

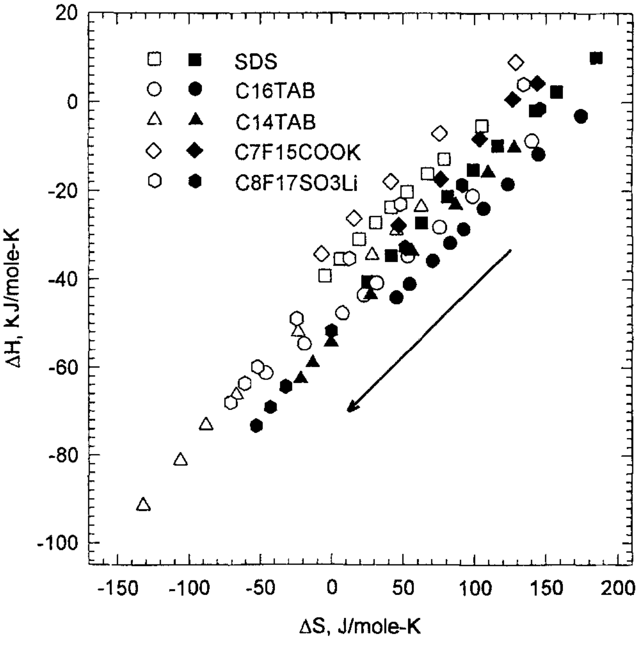
	SDS		$C_{16}TAB$	
T, °C	CMC, 10^{-3} M	β	CMC, 10^{-3} M	β
10	8.81	0.33	1.01	0.23
20	8.48	0.35	0.98	0.25
30	8.44	0.38	1.00	0.27
40	8.89	0.41	1.08	0.29
50	9.62	0.43	1.22	0.31
60	10.5	0.45	1.46	0.32
70	12.3	0.46	1.71	0.34
80	14.0	0.47	2.13	0.35
90	15.9	0.49	2.71	0.37

Based on the Gibbs free energy change in Eqs. (1) or (2), the enthalpy-entropy compensation plot can be plotted, as demonstrated in Fig. 1. Clearly, a parallel relationship holds between different surfactant systems when PS or MA model is applied, and the compensation temperature can be found from the slope. It is found, with finite certainty, that the linearity for enthalpy-entropy curve is held only when the system temperature is low to medium. When temperature is high, all curves concave downwards which gives a larger slope, and also a larger T_c. Similar temperature dependence had been reported previously [15]. The best-fitted T_c's based on data in the linear region are listed in Table 2 and the values are close to those reported previously [15, 18]. No significant difference can be detected for the employment of PS or MA model from these compensation temperatures.

Table 2 CMC_0, T_0, T_c, ΔC_P and ΔS^* for various surfactant systems

surfactant	CMC_0 10^{-3} M	T_0 °C	T_{cP2} °C	T_{cM} °C	ΔC_P J/mol-K	ΔS^* J/mol-K
SDS	8.20	25	321	315	− 620	− 5.6
$C_{16}TAB$	0.90	20	324	318	− 780	− 17
$C_{14}TAB$ [20]	3.79	25	314	325	− 660	− 10
$C_8F_{17}SO_3Li$ [5]	7.80	30	329	322	− 520	9.2
$C_7F_{15}COOK$ [5]	2.65	40	333	320	− 540	6.8

Fig. 1 ΔH versus ΔS. Arrow indicates the increase of temperature



The presence of impurities might lead to considerable CMC-shift and is sensitive in the evaluation of thermodynamic property changes. However, since the data under room temperatures compare well with those available in literature, and since the presence of various impurities should have a profound effect on both the compensation temperature (T_c) and the reference temperature (T^*), the impurity effect is believed to be secondary.

The entropy changes ΔS_{P2} and ΔS_M are plotted against $\ln(T/T^*)$ in Fig. 2, where T^* is 112 °C. The entropy change ΔS_{P1} will be half of ΔS_{P2} and is not shown here for brevity. At temperature T^* the entropy changes for all surfactants are close to zero. On the contrary, the entropy change ΔS_M scatters largely. No general correlation based on T^* can be found [24].

From ΔS_{P2} (and also ΔS_{P1}) and $\ln(T/T^*)$ plot shown in Fig. 2, the heat capacity change and ΔS^* can be found by assuming a constant heat capacity change as follows [14]:

$$\Delta S = \Delta S^* + \Delta C_P \ln(T/T^*)\,. \tag{3}$$

The best-fitted values are listed in Table 2.

The heat capacity changes for $C_{16}TAB$ and $C_{14}TAB$ from ΔS_{P1} (or ΔS_{P2}) are respectively -390 (-780) and -330 (-660) J/mole-K. Causi et al. [25] found that the heat capacity change measured by microcalometric technique for micellization of surfactant $C_{12}TAB$ is about -540 J/mole-K. Since the heat capacity change should be more negative for a longer hydrophobic tail, Eq. (1) with $\gamma = 2$, the neutral micelle model, is a better description than that with $\gamma = 1$, the completely ionized micelle model.

The near-zero ΔS^* is also noticeable. At temperature T^*, the entropy change for all hydrophobic substances dissolution process will be about -80, 0, or 16 J/mole-K if the solute is respectively of gas, liquid or solid state [9]. Due to various head groups and counterions appearing in these surfactant systems, such a result implies that the micelle interior is oil-like [26] and the entropy change for the association of the head group and the counterion is relatively small.

The ΔS_{P2} versus ΔC_P data at 25 °C are plotted in Fig. 3. The data for transfer of gas or liquid hydrocarbons from aqueous solution to its original state, which was discussed in refs. [9, 27], are also shown in the figure for comparison. Although there is some scattering, the correlation between the ionic surfactants and the liquid hydrocarbons is clear.

The heat capacity changes for $C_{14}TAB$ and $C_{16}TAB$ shows an increase of about 60 J/mole-K with an addition of a methylene group, which is close to an average value of 43 J/mole-K reported previously [28]. Due to the very limited data available, this result should be considered to be of preliminary nature.

The temperature dependence of compensation temperature warrants some further discussion. A recent interpretation of the compensation temperature has been proposed by Murphy [14] as follows:

$$T_C = \frac{T - T_H}{\ln(T/T^*)} = \frac{\Delta h_C}{\Delta S_C}\,, \tag{4}$$

Fig. 2 ΔS versus $\ln T/T^*$, $T^* = 112$ °C. Open symbols are for ΔS_{P2} and solid symbols are for ΔS_M

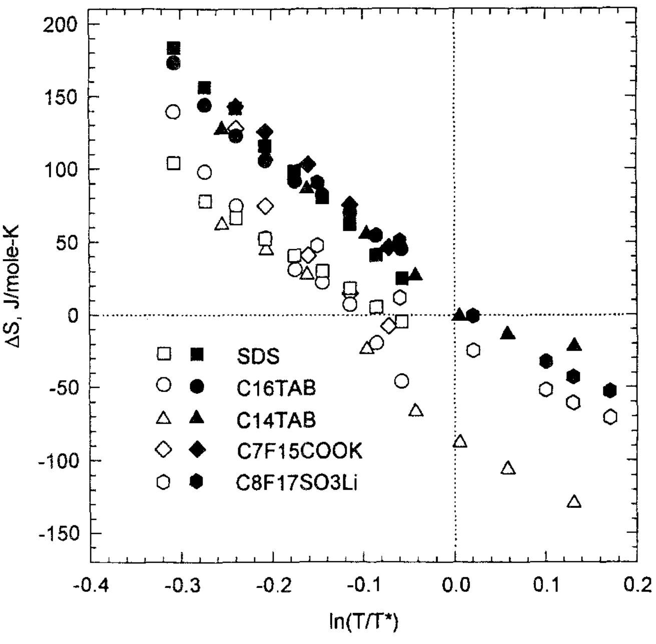
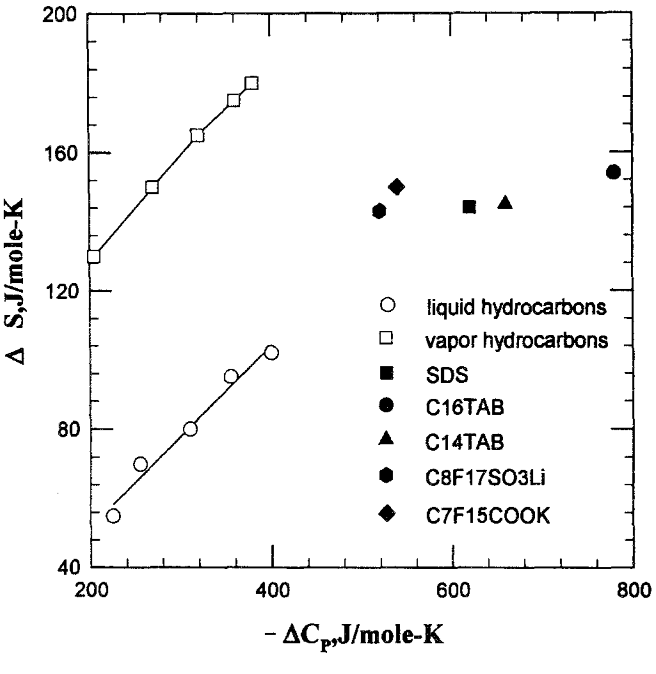


Fig. 3 ΔS versus ΔC_p. 25 °C. The open symbols are for liquid hydrocarbon dissolution process [27]



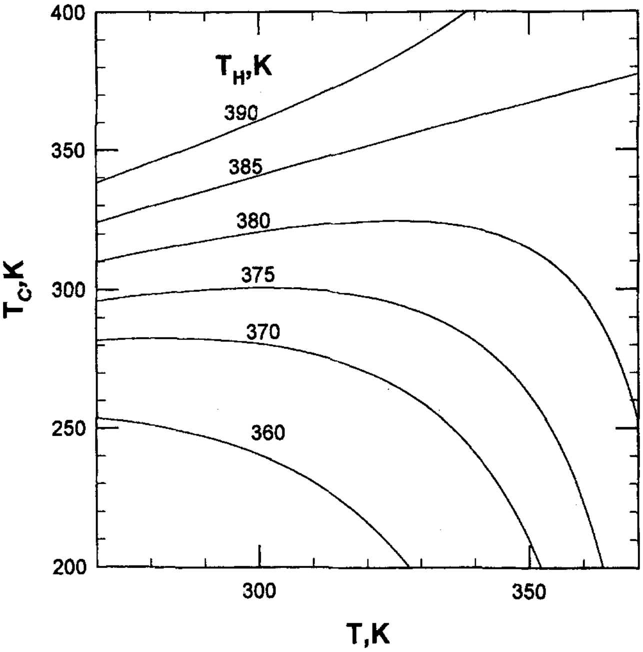


Fig. 4 T_c versus T. $T^* = 112\,°\mathrm{C}$

where Δh_C and ΔS_C are respectively the enthalpy and entropy change for transfer of a methylene group into water, and T is the temperature at which the experiment is made.

Take $T^* = 112\,°\mathrm{C}$; according to Eq. (4) the compensation temperature can be plotted against T with T_H as a parameter, as demonstrated in Fig. 4. Clearly, the compensation temperature will be a near-constant value over a finite range of T, and diverges when T is high. The constant compensation temperature thus obtained is a strong function of T_H, and only when T_H is close to T^*, T_c will be close to room temperature. The calculations by Murphy (1994) also proposed a rather high T_H. Besides, with certain T_H, the compensation plot may possess a higher slope when T is large, which is qualitatively consistent with experiments.

Based on such an interpretation, the enthalpy change due to hydrophobic interaction at T_0, the minimum of CMC-T curve, should be a large positive value. The zero enthalpy change based on PS model at T_0 therefore results from a negative enthalpy change contributed by the association of counterion with the ionized head group on the micelle.

It is hence proposed that the compensation temperature in ionic micellization can be interpreted based on the reference temperatures, which is the same as other hydrophobic processes.

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Notations

ΔC_p	heat capacity change, J/mol-K
CMC	critical micelle concentration, M
CMC_0	critical micelle concentration at $T = T_0$, M
ΔG	Gibbs free energy change, kJ/mol
ΔH	enthalpy chang, kJ/mol
Δh_c	enthalpy change for transfer of a methylene group to water, kJ/mol
R	gas constant, 8.314 J/mol-K
ΔS	entropy change, J/mol-K
ΔS_c	entropy change for transfer of a methylene group to water, J/mol-K
ΔS^*	entropy change at $T = T^*$, J/mol-K
T	temperature, K
T_c	compensation temperature, K
T_H	temperature at which $\Delta H = 0$, K
T_0	temperature at the minimum point, K
T^*	$= 112\,°\mathrm{C}$

Greek Letters

β	degree of dissociation, –

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