

Description of Temperature Dependence of Critical Micelle Concentration

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Received January 29, 2003

A new equation has been derived on the basis of $\Delta G^{\circ} = -RT \ln K$, linear behavior of the enthalpy of micellization with temperature, and the Gibbs-Helmholtz relation. It describes correctly the dependence of critical micelle concentration (X_{CMC}) on temperature and has yielded excellent fitting results for various surfactant systems. The new equation results in the linear behavior of the entropy of micellization with temperature and accounts for the compensation phenomena observed for the micellization in aqueous solutions, along with the linear dependence of the enthalpy of micellization on temperature. These results imply that the new equation of $X_{CMC}(T)$ accounts for the temperature dependence of CMC correctly.

Key Words : Critical micelle concentration, Temperature dependence, Thermodynamic potentials of micellization

Introduction

For ionics and amphoteric, micellization is affected by temperature as the hydrophobic and head group interactions change with temperature. Accordingly, critical micelle concentration (CMC) versus temperature studies have been performed to obtain information on these interactions.¹ For nonionic surfactants, CMC decreases with an increasing temperature due to an increase in hydrophobicity caused by the destruction of hydrogen bonds between water molecules and hydrophilic groups and the log CMC vs. $1/T$ plot is nearly linear.² Meanwhile, for ionic surfactants CMC decreases to a minimum value, characterized by the minimum CMC, X_{CMC}^* , and the temperature, T^* at X_{CMC}^* , and then increases, displaying a U-shaped behavior.^{3,4}

When CMC is measured at various temperatures, the thermodynamic potentials of micellization can be determined.³⁻¹⁰ The standard Gibbs free energy of micellization *per mole of surfactant or amphiphile*, ΔG_{mczn}° , may be obtained from the relation $\Delta G_{mczn}^{\circ} = -RT \ln K/n$ with K and n being the equilibrium constant and association number, respectively, for the micellization. Then, the enthalpy of micellization, ΔH_{mczn}° , is obtained from ΔG_{mczn}° and the Gibbs-Helmholtz relation, $\partial(\Delta G_{mczn}^{\circ}/T)/\partial T = -\Delta H_{mczn}^{\circ}/T^2$ and the entropy of the micellization, ΔS_{mczn}° , from $\Delta S_{mczn}^{\circ} = (\Delta H_{mczn}^{\circ} - \Delta G_{mczn}^{\circ})/T$.

In determining ΔH_{mczn}° from ΔG_{mczn}° and the Gibbs-Helmholtz relation, the temperature dependence of ΔG_{mczn}° should be known so that its partial derivatives with respect to T are calculated. This signifies that X_{CMC} should be described as a function of temperature and this has been done by expressing X_{CMC} as polynomials of temperature. However, such description of $X_{CMC}(T)$ is not theory-based and therefore a theory-based and rigorous equation is

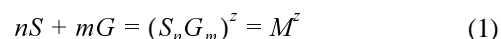
desired.

In this article an equation of $X_{CMC}(T)$ is derived on the basis of $\Delta S_{mczn}^{\circ} = -RT \ln K/n$, linear behavior of $\Delta H_{mczn}^{\circ}(T)$,¹¹⁻¹⁴ and the Gibbs-Helmholtz relation. This equation has been also used in determination of ΔH_{mczn}° by Muller¹⁵ and Singh¹⁶ for specific surfactant systems. We have examined the equation for various surfactant systems and the results are presented.

The equation fits the measured CMC data excellently for surfactant systems. It also accounts for the compensation phenomena,¹⁷⁻²³ which states that ΔS_{mczn}° varies linearly with ΔH_{mczn}° .

Gibbs Free Energy of Micellization and Critical Micelle Concentration (CMC)

Thermodynamics of micellization has been often described by the models of mass action law and phase separation, and the former sheds more light on quantitative understanding of micellization. Let us consider the closed association model because it provides the essence of micellization without loss of generality. The model assumes that micelles comprised of n surfactant molecules are found and that they are formed *via* the reaction:



surfactant counterion micelle

in which z is the charge or the valence of the micelles.

The standard Gibbs free energy change, ΔG° , for the micellization of eq. 1 can be obtained from the well-known thermodynamic result $\Delta G^{\circ} = -RT \ln K$:

$$\Delta G^{\circ} = -RT \ln K = -RT(\ln X_M - n \ln X_S - m \ln X_G). \quad (2)$$

Here the equilibrium constant K for the reaction is

$$K = \frac{a_M}{a_S^n a_G^m} = \frac{X_M}{X_S^n X_G^m} K_{\gamma}, \quad K_{\gamma} \equiv \frac{\gamma_M}{\gamma_S^n \gamma_G^m}. \quad (3)$$

in which $a_i (= \gamma_i X_i)$ is the activity of the species i with γ and

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X being the activity coefficient and mole fraction, respectively, and $K_\gamma = 1$ is assumed. If we define $\Delta G_{m\,c\,z\,n}^o$ as the standard Gibbs free energy change of micellization *per mole of amphiphile*, i.e., $\Delta G_{m\,c\,z\,n}^o = \Delta G^o/n$, then

$$\begin{aligned} \Delta G_{m\,c\,z\,n}^o &= \frac{1}{n}\mu_M^o - \mu_S^o - \frac{m}{n}\mu_G^o \\ &= -\frac{RT}{n}\ln K = -RT\left(\frac{1}{n}\ln X_M - \ln X_S - \frac{m}{n}\ln X_G\right) \quad (4) \end{aligned}$$

in which μ_i^o is the standard chemical potential of species i .

Introducing the ratio $\sigma = X_M/X_{CMC}$ as Tanford did²⁴ and recognizing that, at the CMC, $X_S = X_{CMC} - X_M$ and that $X_G \approx X_S (= X_{CMC})$ when the ionic surfactant $S_{v_S}G_{v_G}$ is like a symmetric electrolyte, i.e., $v_S = v_G$, we obtain

$$\frac{\Delta G_{m\,c\,z\,n}^o}{RT} = \left(1 + \frac{m}{n} - \frac{1}{n}\right)\ln X_{CMC} - \frac{1}{n}\ln \sigma + \ln(1 - \sigma). \quad (5)$$

The choice of σ has only a small effect on the free energy of micellization because it ranges usually from 0.01 to 0.10. Moreover, for large n (for example, $n \geq 50$) the third, fourth, and fifth terms in the right-hand side are negligible. Hence, in this case eq. 5 is reduced to

$$\frac{\Delta G_{m\,c\,z\,n}^o}{RT} = (1 + \beta)\ln X_{CMC}. \quad (6)$$

The fourth and fifth terms of eq. 5 may be elaborated^{22,23} using the fact that physical properties of surfactant solutions change abruptly at the CMC. For a micellar system, the number of degrees of freedom is three. Accordingly, the total surfactant concentration can determine the concentrations of every chemical species at constant temperature and pressure. On the basis of one mole of the total concentration the mass balances for counterions and surfactant ions yield

$$v_S X_{St} = X_S + nX_M \quad (7)$$

$$v_G X_{St} = X_G + mX_M \quad (8)$$

where v_S and v_G are the valences of the surfactant ion and counterion, respectively, of the surfactant $S_{v_S}G_{v_G}$ and X_{St} is the fraction of total surfactant. The CMC can be identified by the Philip's criterion,²⁵ $d^3 B/dX_{St}^3 = 0$. Here B is a property of the micellar solution, which may be represented by

$$B = b_S X_S + b_G X_G + b_M X_M \quad (9)$$

where b_i is the contribution factor of each species and is related to the partial molar quantity of respective species.

After substantial mathematical manipulations²⁶ for $d^3 B/dX_{St}^3 = 0$, one obtains

$$\begin{aligned} \frac{\Delta G_{m\,c\,z\,n}^o}{RT} &= \left[\left(1 + \frac{m}{n} - \frac{1}{n}\right)\ln X_{CMC}\right] + \left[\frac{1}{n}\ln \frac{n(n+m)(2n+2m-1)}{n+m-2}\right] \\ &+ \left[\left(1 + \frac{m}{n} - \frac{1}{n}\right)\ln \frac{1}{v_S} \frac{(n+m)(2n+2m-1)}{(n+m-1)(n+m+1)}\right] \quad (10) \end{aligned}$$

For $n > 50$, the third term in the first bracket and the quantities in the second and third brackets become negligible and eq. 6 is recovered.

Eq. 10 is also employed for the micellization of nonionic amphiphiles, for which $m = 0$ or $\beta = 0$. Therefore it is reduced to

$$\begin{aligned} \frac{\Delta G_{m\,c\,z\,n}^o}{RT} &= \left[\left(1 - \frac{1}{n}\right)\ln X_{CMC}\right] \left[\frac{1}{n}\ln \frac{n^2(2n-1)}{n-2}\right] \\ &+ \left[\left(1 - \frac{1}{n}\right)\ln \frac{1}{v_S} \frac{n(2n-1)}{n^2-1}\right] \quad (11) \end{aligned}$$

Dropping $1/n$ terms in eqs. 10 and 11 makes them reduced further to eqs. 12a and 12b.

$$\begin{aligned} \frac{\Delta G_{m\,c\,z\,n}^o}{RT} &= \left(1 + \frac{m}{n}\right)\ln X_{CMC} + \frac{1}{n}\ln 2n(n+m) \\ &+ \left(1 + \frac{m}{n}\right)\ln \frac{2}{v_S} \quad (\text{for ionics}) \quad (12a) \end{aligned}$$

$$\frac{\Delta G_{m\,c\,z\,n}^o}{RT} = \ln X_{CMC} + \frac{1}{n}\ln 2n^2 + \ln \frac{2}{v_S} \quad (\text{for nonionics}) \quad (12b)$$

For ionics eqs. 6 and 12a are good approximates to eq. 10. Likewise, for nonionics eq. 6 with $\beta = 0$ and eq. 12b are good approximates to eq. 11. Details of mathematical derivation and comparison of terms in eq. 11 are found in reference 27.

Temperature Dependence of Heat of Micellization

Heat of micellization or enthalpy of micellization, $\Delta H_{m\,c\,z\,n}^o$, has been determined in two ways; one is direct measurement with a calorimeter and the other is calculation from $\Delta G_{m\,c\,z\,n}^o$ and the Gibbs-Helmholtz relation.

Direct Method. It has been observed that experimentally measured $\Delta H_{m\,c\,z\,n}^o$ in aqueous surfactant solutions varies linearly with temperature,¹¹⁻¹⁴ namely $\Delta H_{m\,c\,z\,n}^o = A_H T + B_H$, where A_H and B_H are the slope and intercept, respectively, in the $\Delta H_{m\,c\,z\,n}^o$ versus T plot. Figure 1 shows such observations; Figure 1a for 8 hydrocarbon surfactants¹¹ and Figure 1b for perfluoropolyether carboxylic acid and salt (H-, Na-PFPE) and perfluorooctanoic acid and salt (H-, Na-PFO).¹²

Since $\partial \Delta H_{m\,c\,z\,n}^o / \partial T = \Delta C_{p,m\,c\,z\,n}^o$, the slope A_H should be equivalent to $\Delta C_{p,m\,c\,z\,n}^o$, the heat capacity change of micellization. The linearity between $\Delta H_{m\,c\,z\,n}^o$ and T indicates that $\Delta C_{p,m\,c\,z\,n}^o$ is constant at the observed temperature intervals and that, as shown in Figures 1 and 2, $\Delta C_{p,m\,c\,z\,n}^o$ is positive for hydrocarbon surfactants and negative for perfluorinated ionic surfactants. If $\Delta H_{m\,c\,z\,n}^o = 0$ at the (reference) temperature $T_{H=0}$, the linear behavior of $\Delta H_{m\,c\,z\,n}^o$ with T can be stated as

$$\Delta H_{m\,c\,z\,n}^o = \Delta C_{p,m\,c\,z\,n}^o (T - T_{H=0}) \quad (13)$$

The heat capacity change, which is characteristic of the reactions in surfactant systems, is a consequence of solvation

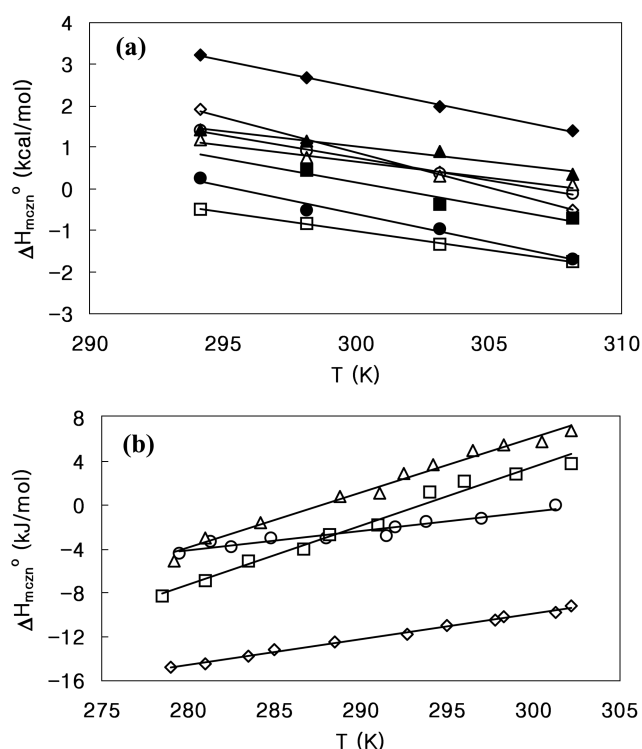


Figure 1. Calorimetric enthalpy change with temperature of micelle formation in various aqueous surfactant solutions. (a) for dimethyldecylphosphine oxide (◆), dimethyldodecylphosphine oxide (◇), sodium dodecyl sulfate (●), sodium dodecoyl sarcosinate (○), sodium octyl sulfate (▲), sodium decyl sulfate (△), dodecylpyridinium bromide (■), dodecylpyridinium chloride (□), and (b) for perfluorinated ionic surfactants, Na-PFPE (◇), H-PFPE (○), Na-PFO (□), H-PFO (△).

and particularly of the structuring of water molecules in the vicinity of surfactant chains related to hydrophobicity, and is normally negative.²⁸

Indirect Method. $\Delta H_{m\,czn}^o$ may be determined from $\Delta G_{m\,czn}^o$ and the Gibbs-Helmholtz equation,

$$\partial(\Delta G_{m\,czn}^o/T)/\partial T = -\Delta H_{m\,czn}^o/T^2. \quad (14)$$

Since dropping $1/n$ terms would cause the error within 0.5%²⁷ eq. 12a can be used as a good approximate for $\Delta G_{m\,czn}^o$. Then one obtains

$$\begin{aligned} \frac{\Delta H_{m\,czn}^o}{R} &= -T^2 \frac{\partial}{\partial T} \left(\frac{\Delta G_{m\,czn}^o}{RT} \right) \\ &= (1 + \beta) \frac{\partial}{\partial T} \ln X_{CMC} + \ln X_{CMC} \frac{\partial}{\partial T} (1 + \beta) + \frac{\partial}{\partial n} f(n; \beta) \frac{\partial n}{\partial T} \\ &= (1 + \beta) \frac{\partial}{\partial T} \ln X_{CMC} + \frac{\partial f(n; \beta)}{\partial n} \frac{\partial n}{\partial T} \end{aligned} \quad (15)$$

where $f(n; \beta)$ is defined as

$$\begin{aligned} f(n; \beta) &= \frac{1}{n} \ln 2n(n + m) + \left(1 + \frac{m}{n} \right) \ln \frac{2}{v_s} \\ &= \frac{1}{n} \ln 2n^2(1 + \beta) + (1 + \beta) \ln \frac{2}{v_s} \end{aligned} \quad (16)$$

The quantity $f(n; \beta)$ is, in principle, a function of n and β ($\equiv m/n$). However, β , the degree of counterion binding, is weakly varying, although oscillatory in some cases,^{10,29} or almost constant with temperature. Hence, $f(n; \beta)$ may be considered as a function of n only and this is reflected in eq. 15.

Determination of $\Delta H_{m\,czn}^o$ by the indirect method has been done usually by using eq. 15 without second term, *i.e.*, neglecting the contribution by the second term $[\partial f(n; \beta)/\partial n]$ $[\partial n/\partial T]$. Some researchers^{30,31} have asserted that such calculation of $\Delta H_{m\,czn}^o$ is not proper because of the large changes in aggregation number that can occur with temperature. However, Krescheck¹¹ and Kiraly¹³ have defended this procedure, chiefly on the ground that the $\Delta H_{m\,czn}^o$ thus calculated agree with the calorimetric estimates.

Temperature Dependence of Critical Micelle Concentration

A new description of the thermal behavior of critical micelle concentration is derived from $\Delta G^o = -RT \ln K$, the linear behavior of $\Delta H_{m\,czn}^o(T)$, and the Gibbs-Helmholtz relation, *i.e.*, from eqs. 12a, 13, and 14. From the last two equations one obtains

$$\Delta G_{m\,czn}^o = c_{const} - \frac{\Delta G_{p,\,m\,czn}^o}{R} \ln T - \frac{\Delta G_{p,\,m\,czn}^o T_{H=0}}{R} \frac{1}{T}. \quad (17)$$

Combining eqs. 12a and 22 now yields

$$\ln X_{CMC} = A + B \ln T + \frac{C}{T} - \frac{1}{(1 + \beta)n} \ln 2n^2(1 + \beta) - \ln \frac{2}{v_s}, \quad (18)$$

where A is a undetermined coefficient, and B and C are defined as

$$B \equiv \frac{-\Delta G_{p,\,m\,czn}^o}{(1 + \beta)R} > 0 \quad (19a)$$

$$C \equiv \frac{-\Delta G_{p,\,m\,czn}^o T_{H=0}}{(1 + \beta)R} > 0 \quad (19b)$$

B and C are positive, since $\Delta G_{p,\,m\,czn}^o$ is negative. $T_{H=0}$ is around a room temperature.

The fourth and the fifth terms of eq. 18 is negligibly small compared to the first three terms and therefore they can be dropped to obtain

$$\ln X_{CMC} = A + B \ln T + \frac{C}{T}. \quad (20)$$

Results and Discussion

Because eq. 20 has three fitting parameters like a 2nd-order polynomial, fits by both equations are examined. Figure 2 shows the results of the fits by these equations for dodecyl-4-methoxypyridinium chloride.⁴ Both equations fit the data well and eq. 20 fits slightly better than the 2nd-order

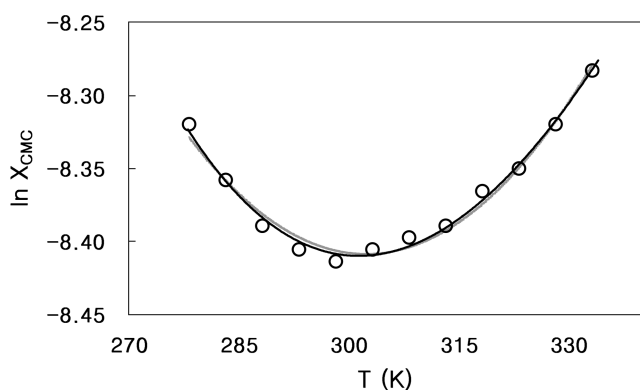


Figure 2. Comparison of 2nd-order polynomial fitting and our equation fitting for dodecyl-4-methoxy pyridinium chloride (gray line: 2nd polynomial fitting, full line: our functional form fitting).

polynomial (correlation coefficients, 0.9958 vs. 0.9883).

Eq. 20 has been employed to fit CMC data of various surfactant systems and it yields the results which are in excellent agreement with the measured data. Figures 3-6 show the results for nonionic n-dodecyl polyethylene glycol monoether ($C_{12}E_4$, $C_{12}E_6$, $C_{12}E_8$),⁸ α -sulfonatomyristic acid methyl ester, ethyl ester,²² cationic alkyltrimethylammonium

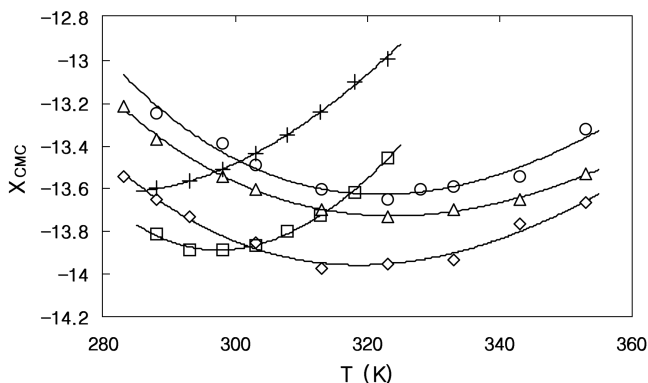


Figure 3. Eq. (20) fitting of nonionic surfactant solutions (\square : $C_{12}E_4$ (correlation coefficient, $r=0.9934$), \diamond : $C_{12}E_6$ ($r=0.9984$), \triangle : $C_{12}E_8$ ($r=0.9899$), \circ : α -sulfonatomyristic acid methyl ester ($r=0.9980$), $+$: α -sulfonatomyristic acid ethyl ester ($r=0.9994$)).

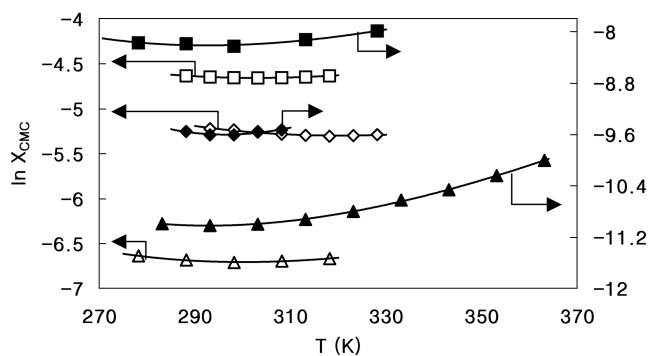


Figure 4. Eq. (20) fitting of cationic surfactant solutions (\square : $i=6$ (correlation coefficient, $r=0.9989$), \diamond : $i=8$ ($r=0.9812$), \triangle : $i=10$ ($r=0.9924$), \blacksquare : $i=12$ ($r=0.9882$), \blacklozenge : $i=14$ ($r=0.9777$), \blacktriangle : $i=16$ ($r=0.9996$)).

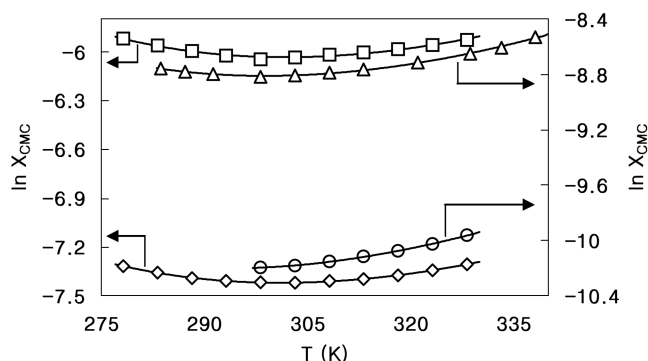


Figure 5. Eq. (20) fitting of anionic surfactant sodium alkyl (\square : octyl (correlation coefficient, $r=0.9866$), \diamond : decyl ($r=0.9992$), \triangle : dodecyl ($r=0.9984$), \circ : tetradecyl ($r=0.9997$)) sulfate solutions.

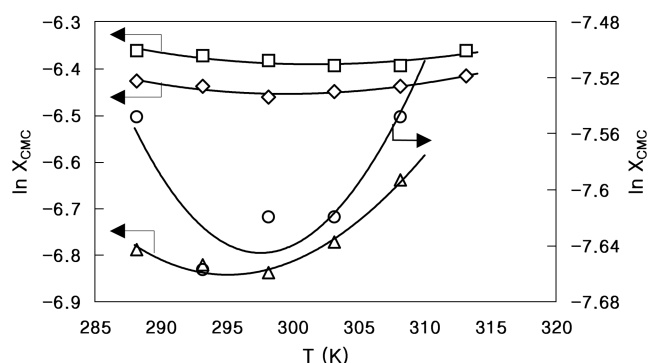


Figure 6. Eq. (20) fitting of amphiphilic drugs (\square : cloxacillin (correlation coefficient, $r=0.9725$), \diamond : dicloxacillin ($r=0.9765$), \triangle : imipramine ($r=0.9913$), \circ : clomipramine ($r=0.9733$)) solutions.

bromide (C_iTAB , $i=6$,³² 8 ,⁹ 10 ,³³ 12 ,³⁴ 14 ,³⁵ 16 ³⁶), anionic (sodium alkyl sulfate, SOS, SDeS, SDS, STS^{3,37,38}) surfactants, and amphiphilic drugs (cloxacillin, dicloxacillin,³⁹ imipramine, clomipramine⁴⁰), respectively. The results in these figures imply that eq. 20 describes correctly the temperature dependence of CMC for most of surfactant systems.

The entropy change, ΔS_{mczn}^o , for the micellization can be obtained from the relation $T\Delta S_{mczn}^o = \Delta H_{mczn}^o - \Delta G_{mczn}^o$. Hence, one obtains

$$\Delta S_{mczn}^o = A_s + \Delta G_{p,mczn}^o \ln T. \quad (21)$$

This equation exhibits the overall behavior as shown in Figure 7. However, the linearity is well perceived above 273.15 K (0 °C) in Figure 7 with correlation coefficient 0.9995, for which aqueous surfactant solutions are examined for micellization.

The linear relationship between ΔS_{mczn}^o and T above 273.15 K can be shown by modifying eq. 21. Eq. 21 can be rewritten as

$$\Delta S_{mczn}^o = A_s \left(1 + \frac{\Delta G_{p,mczn}^o}{A_s} \ln T \right) \quad (21a)$$

Let the reference temperature be T_0 (>273.15 K) and $\delta = T -$

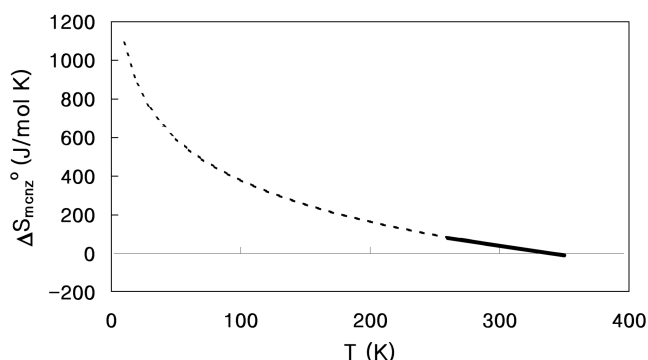


Figure 7. ΔS_{mczn}^o by eq. (21) and the portion at $T > 273$ K for which ΔS_{mczn}^o changes linearly with temperature.

T_0 . Then, this equation becomes

$$\Delta S_{mczn}^o = A_S \left[1 + \frac{\Delta G_{p,mczn}^o}{A_S} \left\{ \ln T_0 + \ln \left(1 + \frac{\delta}{T_0} \right) \right\} \right] \quad (21b)$$

Expanding into a power series yields

$$\ln \left(1 + \frac{\delta}{T_0} \right) = \frac{\delta}{T_0} - \frac{1}{2} \left(\frac{\delta}{T_0} \right)^2 + \frac{1}{3} \left(\frac{\delta}{T_0} \right)^3 - \dots \quad (21c)$$

The first term only is maintained because δ/T_0 is very small. Hence, ΔS_{mczn}^o can be well approximated as

$$\begin{aligned} \Delta S_{mczn}^o &= A_S \left[1 + \frac{\Delta G_{p,mczn}^o}{A_S} \left(\ln T_0 + \frac{\delta}{T_0} \right) \right] \\ &= \alpha_{so} + \frac{\Delta G_{p,mczn}^o}{T_0} T \end{aligned} \quad (22)$$

where α_{so} is defined as

$$\alpha_{so} = A_S + \Delta G_{p,mczn}^o (\ln T_0 - 1). \quad (23)$$

Eq. 22 shows that ΔS_{mczn}^o changes linearly with temperature above 273.15 K.

The corollary of the new equation, eq. 20, is that it accounts for the compensation phenomena, which states that large change in ΔH_{mczn}^o and ΔS_{mczn}^o compensate each other, leaving ΔG_{mczn}^o almost invariant and small in magnitude, and that ΔH_{mczn}^o changes linearly with ΔS_{mczn}^o . The linear behavior of ΔS_{mczn}^o with temperature, eq. 22, is resulted from eq. 20. Combining eq. 22 with eq. 13, observed linear behavior of ΔH_{mczn}^o with T , one obtains

$$\Delta H_{mczn}^o = T_0 \Delta S_{mczn}^o - (T_0 \alpha_{so} + \Delta G_{p,mczn}^o T_{H=0}). \quad (24)$$

This equation clearly shows that ΔH_{mczn}^o changes linearly with ΔS_{mczn}^o or vice versa. The reference temperature T_0 is called the compensation temperature and characterizes the compensation phenomenon. T_0 has been found to be 307 ± 7 K for 11 surfactants²² and this value may be in practice independent of surfactant systems.²³ Figure 8 shows the linearity between ΔH_{mczn}^o and ΔS_{mczn}^o whose values are

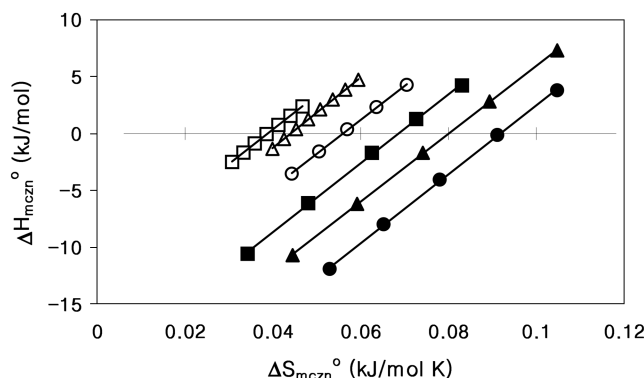


Figure 8. The linearity between ΔH_{mczn}^o and ΔS_{mczn}^o for cationic surfactants C_iTAB (\square : $i=6$, \diamond : $i=8$, \triangle : $i=10$, \blacksquare : $i=12$, \blacklozenge : $i=14$, \blacktriangle : $i=16$).

obtained from calculations by eqs. 15 and 22 for cationic surfactant (C_iTAB , $i = 6,^{32} 8,^9 10,^{33} 12,^{34} 14,^{35} 16^{36}$) systems. Other types of surfactants also exhibit such behavior.⁴¹ This result again manifests strongly that the new equation of $X_{CMC}(T)$ describes correctly the temperature dependence of CMC.

Conclusions

A new equation, $\ln X_{CMC} = A + B \ln T + (C/T)$ has been derived on the basis of $\Delta G^o = -RT \ln K$, linear behavior of the enthalpy of micellization with temperature, and the Gibbs-Helmholtz relation. This equation describes the temperature dependence of critical micelle concentration (CMC), X_{CMC} , with three parameters, A , B , and C . When tested for surfactant systems of various kinds, the equation fits excellently the measured CMC of these surfactant systems. This result may imply that the new equation holds without regard to surfactant systems.

The corollary of the new equation is that the entropy of micellization, ΔS_{mczn}^o , varies linearly with temperature. This result, when combined with the linear behavior of the entropy of micellization, ΔH_{mczn}^o , with temperature, accounts for the compensation phenomena observed for the micellization in aqueous surfactant solutions.

Acknowledgements. H.-U. Kim was gratefully acknowledged to support of the Korea Research Foundation through the grant (No : EN0037).

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