Calorimetric Study of Micelle Formation of Alkylammonium Chlorides in Water

Hideko Sahara^{1*} and Shigeharu Harada²

¹ University of Shizuoka, Junior College, 2-2-1 Oshika, Suruga-ku, Shizuoka-shi, Shizuoka 422-8021, JAPAN

² University of Shizuoka, Emeritus Professor, 5-15-5 Aoinishi, Naka-ku, Hamamatsu-shi, Shizuoka 433-8111, JAPAN

Abstract: Calorimetric measurements were conducted on aqueous solutions of *n*-alkylammonium chlorides (C_nAC ; $H(CH_2)_nNH_3Cl$, $n = 1 - 12$) at 298.15 K. The solute partial molar enthalpy, H_s , was evaluated with reference to the infinitely diluted state. At low concentrations, the H_s increased with the molality, m , until the critical micelle concentration (CMC) was reached. In the concentration range between the CMC and about three times the CMC, the H_s decreased linearly with increasing $\log m$. The H_s observed at the CMC was taken as the enthalpy of micelle formation, ΔH_m , which was expressed as $\Delta H_m / kJ mol^{-1} = 20.1 - 1.4n$ for C_nAC with n from 7 to 12. The Gibbs energy of micelle formation, ΔG_m , was estimated from the CMC values: $\Delta G_m / kJ mol^{-1} = 4.1 - 3.3n$ with n from 5 to 12. The entropy of micelle formation, ΔS_m , was calculated as $T\Delta S_m / kJ mol^{-1} = 16.4 + 1.9n$ with n from 7 to 12. The large positive entropy term was determined to be the driving force for micelle formation. It was inferred that the difference of the CMC of C_nAC and sodium *n*-alkyl sulfate (SC_nS ; $H(CH_2)_nOSO_3Na$, $n = 5 - 13$) homologs seemed to be caused by the difference in the number of possible hydrogen bonds to the head group of the micelle state. Based on an attempt to calculate the H_s for $C_{12}AC$ from the partial molar enthalpy and the concentrations of the constituent individual ions above the CMC, the increase in concentration of the micellar ions seemed to be the largest contribution to the concentration dependence of the H_s .

Key words: isothermal titration calorimetry, partial molar enthalpy, enthalpy of micelle formation, alkylammonium chloride, dodecylammonium chloride, hydrogen bond

1 INTRODUCTION

Isothermal titration calorimetry (ITC) with high precision and sensitivity has recently been used to study the solution properties of surfactants¹⁻¹². From the heat generated during titration, the solute partial molar enthalpies, H_s , were determined as a function of concentration, from which the enthalpy of micelle formation, ΔH_m , was evaluated^{1,3,5-7,9-12}.

We have previously reported the thermodynamic parameters for micelle formation of sodium *n*-alkyl sulfates (SC_nS ; $H(CH_2)_nOSO_3Na$, $n = 5 - 13$) in water at 298.15 K on the basis of the H_s ¹¹ evaluated from ITC data. Large positive changes in entropy were confirmed to be the driving force of micellization.

The present study is an extension of this research. *n*-Alkylammonium chlorides (C_nAC ; $H(CH_2)_nNH_3Cl$, $n = 1 - 12$) were chosen as ionic surfactant homologues of sodium *n*-alkyl sulfates with opposite charge and similar shape. Only a few reports of ΔH_m have been published for alkylam-

monium chlorides^{13,14}.

In this paper, we report a set of data for (1) H_s as a function of molality, m , (2) the critical micelle concentration (CMC) as a function of n , and (3) the enthalpy, ΔH_m , standard Gibbs energy, ΔG_m , and entropy, ΔS_m , of micelle formation as a function of n , and a thermodynamic picture of micelle formation of alkylammonium chlorides will be drawn in comparison to that of sodium alkyl sulfates.

2 EXPERIMENTAL

2.1 Samples

Methylammonium chloride (C_1AC) (purity > 98%) was obtained from Nakarai Chemicals (Kyoto, Japan). Ethylammonium chloride (C_2AC) (purity > 98.0%), *n*-propylammonium chloride (C_3AC) (purity > 98%), *n*-butylammonium chloride (C_4AC) (purity > 98%), and *n*-hexylammonium chloride (C_6AC) (purity > 98%) were obtained from Tokyo

*Correspondence to: Hideko Sahara, University of Shizuoka, Junior College, 2-2-1 Oshika, Suruga-ku, Shizuoka-shi, Shizuoka 422-8021, JAPAN

E-mail: nojima@u-shizuoka-ken.ac.jp

Accepted July 20, 2018 (received for review January 16, 2018)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

Chemical Industry Corporation (Tokyo, Japan). *n*-Pentylamine (purity > 97.0%) and *n*-heptylamine (purity > 99%) were obtained from Kanto Chemical Corporation (Tokyo, Japan) and Acros Organics (Fair Lawn, NJ, USA), respectively. *n*-Pentylammonium chloride (C_5AC) and *n*-heptylammonium chloride (C_7AC) were obtained by neutralization of these *n*-alkylamines dissolved in EtOH with aqueous HCl, and then recrystallized from acetone-EtOH mixtures. The other alkylammonium chlorides were prepared as described in the literature¹⁵⁾. These compounds were vacuum-dried for about one week before use. Water was distilled, deionized by a Milli-Q filtration system, and then degassed by boiling for 30 min before use.

2.2 Measurements

Calorimetric measurements were carried out at 298.15 K on a thermal activity monitor (TAM2277, Thermometric AB, Sweden) controlled by Digitam 4.1 software with static calibrations. The experimental details were reported in our previous paper¹¹⁾.

2.3 Calculation of H_s

We first consider the titration of pure water with a concentrated aqueous solution of the surfactant. A solution composed of n_w^* moles of water and n_s moles of surfactant is injected into n_w^0 moles of pure water, resulting in the generation of heat, Q . When the molality of the surfactant reaches m , equation (1) holds.

$$n_w^0 H_w^0 + n_w^* H_w^* + n_s H_s^* = Q + (n_w^0 + n_w^*) H_w + n_s H_s \quad (1)$$

H_w and H_s are the partial molar enthalpies of water and surfactant in the aqueous solution, respectively, after injection. H_w^0 is the molar enthalpy of pure water, and H_w^* and H_s^* are the partial molar enthalpies of water and surfactant in the concentrated surfactant solution.

On the other hand, the enthalpy change, ΔH_M , caused by the injection of the surfactant solution can be represented by the equation⁷⁾,

$$\Delta H_M = (n_w^0 + n_w^*) H_w + n_s H_s - (n_w^0 H_w^0 + n_w^* H_w^* + n_s H_s^*), \quad (2)$$

which can be compared with equation (1):

$$Q = -\Delta H_M = n_w^0 (H_w^0 - H_w) + n_w^* (H_w^* - H_w) + n_s (H_s^* - H_s) \quad (1')$$

The heat, Q , generated when a solution (of molality m) is made by mixing pure water and the concentrated solution can be calculated by integrating the P vs. t curve at concentrations below the molality m , where P is the heat power corresponding to the temperature change inside the measurement cell, and was recorded as a function of time (t) for every injection of a surfactant solution for time intervals long enough to reach thermal equilibrium.

The mole ratio of water and surfactant in the injected concentrated solution is represented by k^* ,

$$k^* = \frac{n_w^*}{n_s} \quad (3)$$

When Q is differentiated with respect to n_s , the equation

$$\left(\frac{\partial Q}{\partial n_s}\right)_{T,p} = k^* H_w^* + H_s^* - k^* H_w - H_s \quad (4)$$

is obtained on the basis of the Gibbs-Duhem equation (5):

$$(n_w^* + n_w^0) \left(\frac{\partial H_w}{\partial n_s}\right)_{T,p} + n_s \left(\frac{\partial H_s}{\partial n_s}\right)_{T,p} = 0 \quad (5)$$

When $\left(\frac{\partial Q}{\partial n_s}\right)_{T,p}$ is plotted with respect to m , a good linear relationship is obtained in the very low concentration region. This straight line can be extrapolated to infinite dilution to determine the limiting value, H^∞ , thus permitting the calculation of H_s :

$$H^\infty = \lim_{n_s \rightarrow 0} \left(\frac{\partial Q}{\partial n_s}\right)_{T,p} = k^* H_w^* + H_s^* \quad (6)$$

Combining equations (4) and (6), we obtain:

$$H_s = H^\infty - \left(\frac{\partial Q}{\partial n_s}\right)_{T,p} - k^* H_w \quad (7)$$

Here, experiments were carried out for two or more values of k^* . If the value of $[H^\infty - \left(\frac{\partial Q}{\partial n_s}\right)_{T,p}]$, plotted with respect to m , is extrapolated to $k^* = 0$, H_s can be determined.

3 RESULTS

3.1 Relationship between m_t and H_s

Figure 1 shows the concentration dependence of H_s for the $C_{10}AC$ -water system. The plot of H_s vs. m_t is characterized by a large increase at low concentrations followed by a gradual decrease. This characteristic behavior of H_s was also observed for the C_nAC ($n = 5 - 9, 11, 12$)-water systems. The CMC is defined as the concentration given at the intersection of two lines: a line extrapolated from the H_s vs. m_t plot near the intersection, and a linear regression line calcu-

Fig. 1 Dependence of the partial molar enthalpy (H_s) of the $C_{10}AC$ -water system on the surfactant concentration (m_t) at 298.15 K.

Fig. 2 Dependence of the partial molar enthalpy (H_s) of the C_4AC -water system on the surfactant concentration (m_t) at 298.15 K.

lated from the plot of decreasing H_s vs. $\log m_t$, as will be shown in equation (11). Such increases in H_s at concentrations just below the CMC have been reported for nonionic^{3-7,9)} and anionic¹¹⁾ surfactant systems.

For C_nAC ($n = 1 - 4$) aqueous solutions, the plot of H_s vs. m_t did not show a bend indicating the CMC. Instead, H_s increased linearly with increasing m_t over the whole measured range of concentration. The plot of H_s vs. m_t for the C_4AC -water system is shown in **Fig. 2** as a typical example for systems without a CMC.

3.1.1 H_s at concentrations below the CMC

The value of H_s was positive and increased linearly with m_t in the concentration range from zero to the CMC for C_nAC ($n = 5 - 7$) systems and from zero to about three-fourths of the CMC for C_nAC ($n = 8 - 12$) systems.

The value of H_s can be simply expressed as a straight line with a slope of a ,

$$H_s = a m_t \quad (8)$$

As an example, a linear plot for the $C_{10}AC$ solution is shown in **Fig. 1**. **Figure 3** displays the relationship between the chain-length, n , and slope, a , which can be expressed by equation (9).

$$a = 0.1n^3 - 0.6n^2 + 2.2n - 1.8 \quad (9)$$

The addition of a methylene group to C_nAC in the monodisperse state caused an increase in heat absorption with increasing n . The concentration dependence of H_s of C_nAC was similar to that of the ionic surfactant SC_nS ¹¹⁾.

In the concentration range between three-fourths of the CMC and the CMC, a larger increase in H_s was observed for the C_nAC ($n = 8 - 12$)-water systems, as seen in **Fig. 1**, as well as for the SC_nS ($n = 5 - 13$) systems¹¹⁾. It should be noted here that the H_s of nonionic surfactants did not show a dependence on concentrations of monodisperse states below the CMC^{3,7,9)}.

Fig. 3 Parameters for the expression of H_s for C_nAC : a , d , and e . $\blacklozenge$; a in equation (8), $\bullet$; d in equation (11), $\square$; e in equation (11), a was expressed in (kJ/mol)/(mol/kg), d and e were expressed in kJ/mol.

3.1.2 CMC

The increase in H_s at low concentrations turned into a decrease when micelles were formed.

It is well known that equation (10) describes the relationship between the CMC and the number of carbon atoms (n) in surfactant homologs:

$$\log(\text{CMC}) = b - c n \quad (10)$$

Here, b and c are empirical constants; for ionic surfactants the value of c was reported to be approximately 0.3¹⁶⁾, which means that the CMC decreases by about one-half upon the addition of CH_2 group to the surfactant chain. The C_nAC systems were found to be linear and the values of b and c were determined to be 2.01 and 0.31, respectively. Literature values^{13,15,17-25)} of the CMCs for C_nAC are tabulated in **Table 1**. The CMC values obtained from the present calorimetric measurements are shown in **Table 2**; they are somewhat larger than those obtained from other methods. The b and c values found here are comparable to those of SC_nS ($n = 5 - 13$) ($b = 1.62$ and $c = 0.31$) previously reported¹¹⁾.

Figure 4 shows a plot of the logarithm of CMC values of the C_nAC and SC_nS surfactants against the chain-length of the hydrophobic groups (n). Detailed discussions of the differences in the CMCs of both homologs are presented in section 4.1.

3.1.3 H_s at concentrations above the CMC

The plot of H_s vs. $\log m_t$ exhibits a linear relationship as shown in **Fig. 5**.

$$H_s = d - e \log m_t \quad (11),$$

Equations (12) and (13) were obtained from the plot of d and e against n as shown in **Fig. 3**.

$$d = 20.0 - 1.7n \quad (12)$$

Table 1 Literature values of CMC for C_nAC at 298.15K. *; Data obtained in mol L⁻¹.

n	CMC / mol kg ⁻¹	ref No	n	CMC / mol kg ⁻¹	ref No
5	1.9*	17	10	0.048	15
6	0.9*	25		0.04	25
	1*	17		0.045	
7	0.426	24		0.0540	21
	0.45*	17		0.054*	
8	0.175*	25	12	0.0133* ± 0.001	13
	0.24	15		0.014	15
	0.27*	17		0.0146	25
	0.27*	23		0.0147	
9	0.11	15		0.0147*	21
	0.134 (30°C)	20		0.0148	18
11	0.026	15		0.015*	19
				0.015*	22

Table 2 CMC, thermodynamic parameters of micelle formation (ΔH_m , ΔG_m , and $T\Delta S_m$) in this study, and calculated values of the micelle aggregation number (*N*) for C_nAC.

<i>n</i>	CMC / mol kg ⁻¹	ΔH_m / kJ mol ⁻¹	ΔG_m / kJ mol ⁻¹	$T\Delta S_m$ / kJ mol ⁻¹	<i>N</i> calcd. values
5	2.7	9.1	-12.4	21.5	12
6	1.3	9.5	-15.8	25.3	18
7	0.64	9.7	-19.2	28.9	24
8	0.31	8.8	-22.9	31.6	32
9	0.15	7.7	-25.8	33.5	40
10	0.071	6.2	-29.5	35.7	50
11	0.035	4.5	-32.5	37.1	60
12	0.017	2.7	-35.7	38.3	72

$$e = 5.6 - 0.3n \quad (13)$$

As a result, at concentrations above the CMC for $5 \leq n \leq 12$, H_s can be expressed as a function of $\log m_t$ and n :

$$H_s = 20.0 - 1.7n - (5.6 - 0.3n) \log m_t \quad (14)$$

3.2 Thermodynamic parameters of micelle formation

3.2.1 Determination of ΔH_m

The heat of micelle formation, ΔH_m , is defined as the H_s at the CMC. The values of ΔH_m are provided in **Table 2** and plotted against the chain-length (n) in **Fig. 6**. Although our value of 2.7 kJ mol⁻¹ for C₁₂AC was larger than the literature values of 1.5 ± 0.1 ¹³⁾ and 0.67 ¹⁴⁾ kJ mol⁻¹, the chain-length dependence of the present ΔH_m data seems plausible enough, as shown in **Fig. 6**. The ΔH_m value can be described

by equation (15) for $7 \leq n \leq 12$.

$$\Delta H_m / \text{kJ mol}^{-1} = 20.1 - 1.4n \quad (15)$$

The slope of equation (15) indicates that ΔH_m changed by -1.4 kJ mol⁻¹ upon micellization for every methylene group added. A similar value of ΔH_m (-1.7 kJ mol⁻¹) was reported previously for SC_nS¹¹⁾. It was therefore reconfirmed that the exotherm resulting from thermal stabilization due to the aggregation of the hydrophobic groups is larger than the endotherm resulting from the release of hydrophobically hydrated water molecules; thus, the micelle formation for methylene groups is exothermic.

3.2.2 Determination of ΔG_m and $T\Delta S_m$

ΔH_m is the enthalpy with reference to infinite dilution (H_s is zero at $m_t / \text{mol kg}^{-1} = 0$). The standard Gibbs energy, ΔG_m , with reference to infinite dilution was calculated from

Fig. 4 Dependence of the log CMC of C_nAC and SC_nS aqueous systems on the alkyl chain-length (n) at 298.15 K.

Fig. 5 The relationship between H_s and $\log m_t$ at concentrations above the CMC at 298.15 K.

equation (16)²⁶⁾:

$$\Delta G_m = (1 + \beta)RT \ln X_{CMC} + (RT/N) \ln [2N(N+m)] \quad (16)$$

where X_{CMC} is the CMC value expressed in terms of the mole fraction at temperature T , and R is the gas constant. β is the degree of counterion binding: $\beta = m/N$, where N is the micelle aggregation number and m is the number of counterions bound to the micellar surface. The values of β and N for C_nAC ($n = 8-12$) have already been reported¹⁵⁾. Since the β values seem to be invariant with respect to chain-length, the mean value of 0.80 was assumed for the β of C_nAC ($n = 5-7$). The N for C_nAC ($n = 5-7$) was evaluated according to the procedure previously reported¹¹⁾. These values are listed in Table 2; the N values for C_nAC ($n = 6-8$) were comparable to those reported in the literature^{24, 27)}.

The entropy of micelle formation, ΔS_m , was calculated from equation (17):

Fig. 6 Thermodynamic parameters for micelle formation for C_nAC and SC_nS at 298.15 K.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (17)$$

The thermodynamic parameters thus evaluated are plotted against n in Fig. 6 together with those for SC_nS ($n = 5-13$); both systems showed very similar chain-length dependence. Equations (18) and (19) were used to describe ΔG_m ($n = 5-12$) and $T\Delta S_m$ ($n = 7-12$), respectively.

$$\Delta G_m / \text{kJ mol}^{-1} = 4.1 - 3.3 n \quad (18)$$

and

$$T\Delta S_m / \text{kJ mol}^{-1} = 16.4 + 1.9 n \quad (19)$$

ΔH_m was small and corresponded to an endothermic process ($9.7 \sim 2.7 \text{ kJ mol}^{-1}$), whereas ΔG_m was negative and became more negative with increasing chain-length. Consequently, $T\Delta S_m$ had large positive values that increased with n , indicating that entropy is the driving force for micelle formation.

However, it should be noted that the ΔH_m , $T\Delta S_m$, and ΔG_m values of C_nAC changed by -1.4 , 1.9 , and -3.3 kJ mol^{-1} , respectively, upon micellization for every methylene group added. As mentioned in section 3.2.1, the negative ΔH_m per methylene group is attributed to the enthalpic stabilization resulting from the aggregation of hydrophobic groups. On the other hand, the $T\Delta S_m$ per methylene group is positive due to the release of hydrophobically hydrated water molecules on micellization. The $T\Delta S_m$ of every methylene group contributed to lowering the Gibbs energy of micelle formation more than the micellization enthalpy.

4 DISCUSSION

4.1 CMC values of the C_nAC and SC_nS

The logarithms of the CMC values of the C_nAC and SC_nS systems are plotted against the alkyl chain-length (n) in Fig. 4. The CMC values of the former homologues were ap-

proximately twice those of the latter ones at the same n . The order of increasing CMC in alkyl surfactants, $\text{SC}_n\text{S} < \text{sodium alkylsulfonate} < \text{sodium alkylcarboxylate} < \text{C}_n\text{AC}$, can be explained by the increase of electrostatic self-potential of the surfactant ions when the ionic head group moves from the bulk water to the vicinity of micellar α -methylene groups existing in the water-free region²⁸⁾.

However, some remarks should be made on water penetration into micelles. It was reported based on fluorescence quenching experiments²⁹⁾ that in SC_{12}S micelles, water seemed to penetrate further down to the β carbon of the surfactant. Molecular dynamics simulation results³⁰⁾ have also shown a micellar region of SC_{12}S (10 Å portion from $R = 12$ Å to $R = 22$ Å, where R is the distance from the micelle center of mass) where the hydrocarbon and water are in contact.

The radial distribution function of water oxygens-to-micelle oxygens of SC_{12}S revealed that the number of water molecules in the first coordination shell was 0.6 for the O atom between the methylene group and S atom, and 1.3 for the other three O atoms³⁰⁾. It was found in the first shell of the micelle³⁰⁾ that (1) five to seven water molecules were hydrogen-bonded to an individual headgroup ($-\text{OSO}_3^-$) of 70% surfactant monomers, (2) 60% of the water molecules had one micelle-to-water hydrogen bond, and (3) 7% of water molecules formed two hydrogen bonds with two different dodecyl sulfate monomers. The second hydrogen bond between a water monomer and an $-\text{OSO}_3^-$ group gives some additional stability to the micelle³¹⁾.

Although the hydrophilic head of C_{12}AC , $-\text{NH}_3^+$, forms hydrogen bonds of the type $-\text{N}-\text{H} \cdots \text{OH}_2$, the maximum possible number is probably three, which is smaller than that of the hydrophilic head of SC_{12}S ($-\text{OSO}_3^-$), and a second hydrogen bond cannot be made. If a single hydrogen bond between water and the ionic head is maintained on micellization, the formation of a second hydrogen bond might be one of the reasons for the lower CMC of SC_{12}S as compared to C_{12}AC .

4.2 Calculation of H_s

The H_s of C_{12}AC was estimated from the partial molar enthalpy values of the ionic species on the basis of the mass action model of micelle formation^{26, 32–34)}.

There are three kinds of ionic species in an aqueous micellar solution of an ionic surfactant: surfactant ion, counterion, and micelle ion. In C_nAC micelle solutions, there were n -alkylammonium ions, chloride ions, and micelle ions consisting of N n -alkylammonium ions and m chloride ions.

When the C_{12}AC surfactant concentration changes by a value of dm_t , the concentration of the individual species changes by values of dm_{DA} , dm_{Cl} , and dm_{M} . The enthalpy change (dH) equals the sum total of the enthalpy changes of each species in the solution.

$$dH = H_s dm_t = H_{\text{DA}} dm_{\text{DA}} + H_{\text{Cl}} dm_{\text{Cl}} + H_{\text{M}} dm_{\text{M}} \quad (20)$$

where H_{DA} , H_{Cl} , and H_{M} are values of partial molar enthalpy of n -dodecylammonium ions, chloride ions, and micelle ions. Equation (20) can be rewritten as equation (21).

$$H_s = H_{\text{DA}} \frac{dm_{\text{DA}}}{dm_t} + H_{\text{Cl}} \frac{dm_{\text{Cl}}}{dm_t} + H_{\text{M}} \frac{dm_{\text{M}}}{dm_t} \quad (21)$$

On the basis of the mass action model of micelle formation^{26, 32)}, the molar concentrations of the solute ions (m_{DA} , m_{Cl} , and m_{M}) and the micellization constant, K_N , in C_{12}AC micelle solutions were estimated using equations presented by Moroi^{33, 34)}. Figure 7 shows m_{DA} , m_{Cl} , and m_{M} plotted against m_t in C_{12}AC micelle solutions. The symbols and lines showed the concentrations calculated on the assumption that the N increased linearly with m_t ; $N = 72$ ¹⁵⁾ at CMC and $N = 108$ ¹⁹⁾ at $m_t = 0.1 \text{ mol kg}^{-1}$.

Assuming that the partial molar enthalpy values of the solutes are constant within a very narrow concentration range, the values of H_{DA} , H_{Cl} , and H_{M} were determined by means of solving the simultaneous linear equations (21) which hold at three adjacent points of concentration. As shown in Fig. 8, the H_{DA} and H_{Cl} were almost independent of m_t , whereas the value of H_{M} seemed to decrease greatly with increasing m_t . The large H_{M} value was ascribed to the calculation on the basis of the concentration of the aggregates composed of N surfactant ions and m chloride ions. The H_{M}/N values were similar to those of the surfactant ion and counterion. Figure 9 shows the H_s and the contributions of three terms of the single surfactant ion, chloride ion, and micelle ion on the right-hand side of equation (21). In this model, the negative slope of H_s above the CMC seemed to be caused by the formation of the micelle ions.

Fig. 7 The calculated concentrations of n -dodecylammonium ion (m_{DA}), chloride ion (m_{Cl}), and micelle ion (m_{M}) against m_t in C_{12}AC micelle solutions.

Fig. 8 Partial molar enthalpies of *n*-dodecylammonium ion (H_{DA}), chloride ion (H_{Cl}), and micelle ion (H_M) and the value of H_M/N vs. total concentration (m_t) of $C_{12}AC$.

Fig. 9 The observed H_s and the contributions of three terms of the single surfactant ion, chloride ion, and micelle ion in equation (21).

5 CONCLUSION

The partial molar enthalpy of *n*-alkylammonium chloride, $H(CH_2)_nNH_3Cl$ ($n = 1 - 12$), was determined in water at 298.15 K. The thermodynamic parameters of micelle formation (ΔH_m , ΔG_m , and ΔS_m) were determined and expressed as linear functions of n : $\Delta H_m / \text{kJ mol}^{-1} = 20.1 - 1.4n$ in the range $7 \leq n \leq 12$; $\Delta G_m / \text{kJ mol}^{-1} = 4.1 - 3.3n$ in the range $5 \leq n \leq 12$; $T\Delta S_m / \text{kJ mol}^{-1} = 16.4 + 1.9n$ in the range $7 \leq n \leq 12$. The large positive entropy change was confirmed to be the driving force for micelle formation. The chain-length dependence of the thermodynamic parameters of these cationic surfactants was similar to that of sodium *n*-alkyl sulfates, anionic surfactants previously examined¹¹⁾.

The ΔH_m , ΔG_m , and $T\Delta S_m$ per methylene group (-1.4 , -3.3 , and 1.9 kJ mol^{-1}) strongly suggest that both the enthalpic stabilization in aggregation of hydrophobic groups and the entropic stabilization owing to the release of hydrophobically hydrated water molecules occurred during

micellization. The $T\Delta S_m$ contributed to the lowering of ΔG_m more than the ΔH_m .

In $C_{12}AC$ micelle solutions, H_{DA} and H_{Cl} (partial molar enthalpy, H , of *n*-dodecylammonium ions and chloride ions) were almost independent of m_t (the molality of $C_{12}AC$), whereas the H_M (H of micelle ion) showed a large decrease with increasing m_t . The negative slope of H_s (H of $C_{12}AC$) above the CMC was caused by micelle ions.

References

- Desnoyer, J.E.; Perron, G. Thermodynamic properties of surfactant solutions. in *Handbook of Surface and Colloid Chemistry* (Birdi, K.S. ed.), CRC Press, New York, pp. 119-156 (1997).
- Ohta, A.; Takiue, T.; Ikeda, N.; Aratono, M. Calorimetric study of dilute aqueous solutions of ethylene glycol oligomers. *J. Phys. Chem. B*, **102**, 4809-4812 (1998).
- Olofsson, G. Calorimetric studies of the association of amphiphiles in aqueous and nonaqueous solutions. *Netsu Sokutei* **19**, 76-85 (1992).
- Mazer, N.A.; Olofsson, G. Calorimetric studies of micelle formation and micellar growth in sodium dodecyl sulfate solutions. *J. Phys. Chem.* **86**, 4584-4593 (1982).
- Andersson, B.; Olofsson, G. Calorimetric study of non-ionic surfactants. enthalpies and heat-capacity changes for micelle formation in water of C_8E_4 and Triton X-100 and micelle size of C_8E_4 . *J. Chem. Soc., Faraday Trans. 1* **84**, 4087-4095 (1988).
- Wang, G.; Olofsson, G. Ethyl(hydroxyethyl) cellulose and ionic surfactants in dilute solution. Calorimetric and viscosity study of the interaction with SDS and some cationic surfactants. *J. Phys. Chem.* **99**, 5588-5596 (1995).
- Ohta, A.; Murakami, R.; Takiue, T.; Ikeda, N.; Aratono, M. Calorimetric study of micellar solutions of pentaethylene glycol mono-octyl and mono-decyl ethers. *J. Phys. Chem. B* **104**, 8592-8597 (2000).
- Olofsson, G. Microtitration calorimetric study of the micellization of three poly(oxyethylene) glycol dodecyl ethers. *J. Phys. Chem.* **89**, 1473-1477 (1985).
- Aratono, M.; Ohta, A.; Ikeda, N.; Matsubara, A.; Motomura, K.; Takiue, T. Calorimetry of surfactant solutions. Measurement of the enthalpy of mixing of tetraethylene glycol mono-octyl ether and water. *J. Phys. Chem. B* **101**, 3535-3539 (1997).
- Bijma, K.; Engberts, J.B.F.N.; Haandrikman, G.; Van Os, N.M. Blandamer, M.J.; Butt, M.D.; Cullis, P.M. Thermodynamics of micelle formation by 1-methyl-4-alkylpyridinium halides. *Langmuir* **10**, 2578-2582 (1994).
- Sahara, H.; Harada, S. Calorimetric study of micelle

- formation of sodium alkyl sulfates in water. *J. Oleo Sci.* **62**, 1041-1047 (2013).
- 12) Chakraborty, I.; Moulik, S.P. Self-aggregation of ionic C₁₀ surfactants having different headgroups with special reference to the behavior of decyltrimethylammonium bromide in different salt environment: A calorimetric study with energetic analysis. *J. Phys. Chem. B* **111**, 3658-3664 (2007).
 - 13) Loh, W.; Teixeira, L.A.C.; Lee, L-T. Isothermal calorimetric investigation of the interaction of poly(*N*-isopropylacrylamide) and ionic surfactants. *J. Phys. Chem. B* **108**, 3196-3201 (2004).
 - 14) De Lisi, R.; Fiscaro, E.; Milioto, S. Thermodynamic properties and conductivities of some dodecyl surfactants in water. *J. Solut. Chem.* **17**, 1015-1041 (1988).
 - 15) Sahara, H.; Harada, S. Determining the degree of counterion binding to aqueous alkylammonium chloride micelles by an electrode method. *J. Oleo Sci.* **65**, 861-865 (2016).
 - 16) Myers, D. *Surfactant Science and Technology*. 3rd ed. John Wiley & Sons, New Jersey, p. 132 (2006).
 - 17) Kaatze, U. Kinetics of micelle formation and concentration fluctuations in solutions of short-chain surfactants. *J. Phys. Chem. B* **115**, 10470-10477 (2011).
 - 18) Miyagishi, S. The effect of organic additives on the thermodynamic parameters of micellization. *Bull. Chem. Soc. Jpn.* **49**, 34-37 (1976).
 - 19) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. Temperature dependence of the micelle aggregation number and rate of intramicellar excimer formation in aqueous surfactant solutions. *J. Phys. Chem.* **89**, 2709-2713 (1985).
 - 20) Ballesteros, M.; Coronel, C.; Galera-Gómez, P.A. Study of the aggregation of nonylammonium chloride in aqueous solutions of sodium chloride by vapor pressure osmometry. *Colloids. Surf. A Physicochem. Eng. Asp.* **150**, 143-149 (1999).
 - 21) Okamoto, T.; Tsubone, K.; Tajima, K.; Fukada, K. in *The Handbook of Oil Chemistry*. 4th ed. – *Lipids and Surfactants* –, Japan Oil Chemists' Society, ed., Maruzen, Tokyo, p. 552 (2001).
 - 22) Malliaris, A.; Lang, J.; Zana, R. Micellar aggregation numbers at high surfactant concentration. *J. Colloid Interface Sci.* **110**, 237-242 (1986).
 - 23) Polacek, R.; Kaatze, U. Micelle and oligomer kinetics in aqueous solutions of *n*-octylammonium chloride: Monomer exchange, protrusion and chain isomerization. *J. Mol. Liq.* **157**, 125-132 (2010).
 - 24) Telgmann, T.; Kaatze, U. On the kinetics of the formation of small micelles. 1. Broadband ultrasonic absorption spectrometry. *J. Phys. Chem. B* **101**, 7758-7765 (1997).
 - 25) Mukerjee, P.; Mysels, K.J. *Critical Micelle Concentration of Aqueous Surfactant Systems*. NSRDS-NBS 36, National Bureau of Standards, Washington, D.C. (1971).
 - 26) Sugihara, G. Chemical thermodynamics of micellization of surfactants in water. *Dojin News* **95**, 1-9 (2000).
 - 27) Adair, D.A.W.; Hicks, J.R.; Jobe, D.J.; Reinsborough, V. C. Micellar aggregation numbers of short-chained ionic surfactants through viscosity measurements. *Aust. J. Chem.* **36**, 1021-1025 (1983).
 - 28) Stigter, D.; Micelle formation by ionic surfactants. II Specificity of head groups, micelle structure. *J. Phys. Chem.* **78**, 2480-2485 (1974).
 - 29) Melo, E.C.C.; Costa, S.M.B.; Maçanita, A.L.; Santos, H.; The use of the *n*-(9-Anthroyloxy) stearic acids to probe the water content of sodium dodecyl sulfate, dodecyltrimethylammonium chloride, and Triton X-100 micelles. *J. Colloid Interface Sci.* **141**, 439-453 (1991).
 - 30) Bruce, C.D.; Senapati, S.; Berkowitz, M.L.; Perera, L.; Forbes, M.D.E. Molecular dynamics simulations of sodium dodecyl sulfate micelle in water: The behavior of water. *J. Phys. Chem. B* **106**, 10902-10907 (2002).
 - 31) Dastidar, S.G.; Mukhopadhyay, C. Anomalous behavior of water around sodium dodecyl sulphate micelles. *Phys. Rev. E* **70**, 061901 (2004).
 - 32) Moroi, Y. *Micelles: Theoretical and Applied Aspects*. Plenum Press, New York, pp. 47-61 (1992).
 - 33) Moroi, Y. Mass action model of micelle formation: Its application to sodium dodecyl sulfate solution. *J. Colloid Interface Sci.* **122**, 308-314 (1988).
 - 34) Moroi, Y. Physical chemistry of surfactant solutions. *Hyomen* **43**, 616-628 (2005).