

## Effect of the *N*-Methylation of Dodecylammonium Chloride on the Adsorption from Its Micellar Solution

Makoto ARATONO,\* Toru OKAMOTO, Norihiro IKEDA, and Kinsi MOTOMURA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812

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The surface tension of the aqueous solution of dodecylmethylammonium chloride (DMAC) and dodecyl-dimethylammonium chloride (DDAC) was measured as a function of temperature under atmospheric pressure at concentrations below and above the critical micelle concentration (cmc). The entropy and energy of adsorption from the monomeric state in the aqueous solution and the micellar state were evaluated by applying the thermodynamic equations of adsorption to the surface tension values. The thermodynamic quantities were compared with those of the aqueous solutions of dodecylammonium chloride (DAC) and dodecyltrimethylammonium chloride (DTAC). It was found that the successive *N*-methylation of DAC has a considerable effect on the adsorbed film with changes in its surface density, entropy, and energy brought about by changes in the geometry and the hydrophilicity of the polar head group.

The adsorption of dodecylammonium chloride (DAC) and dodecyltrimethylammonium chloride (DTAC) from their micellar solution at water/air interface has been investigated in our previous papers.<sup>1,2)</sup> It has been shown that the thermodynamic quantity changes associated with the adsorption and micelle formation are greatly influenced by the chemical structure of the head group; for example, both entropy changes associated with adsorption from the monomeric state in the solution and the micellar state were negative for DAC and positive for DTAC, while the corresponding energy changes were positive for the two surfactants.

Now the systematic study is required on the effect of the chemical structure of the head group on the adsorption and micelle formation. In this paper we are concerned with the effect of the successive *N*-methylation of dodecylammonium chloride on the adsorption and micelle formation; the adsorption of dodecylmethylammonium chloride (DMAC) and dodecyl-dimethylammonium chloride (DDAC) at the aqueous solution/air interface at concentrations around the critical micelle concentrations is investigated in detail. The surface tension is measured as a function of temperature at fixed concentrations under atmospheric pressure. The thermodynamic quantities are evaluated by applying the thermodynamic equations developed previously<sup>1)</sup> to the measured values of surface tension. By comparing the results with those of DAC and DTAC, the influence of the chemical structure of the head group is considered systematically.

### Experimental

To synthesize dodecylmethylammonium chloride, dodecylmethylamine was prepared first according to the following way.<sup>3)</sup> Acrylonitrile and dodecylamine were mixed slowly, stirred for 30 minutes, and refluxed for six hours. After removal of the excess acrylonitrile in vacuo, resulting *N*-(2-cyanoethyl)dodecylamine was obtained by the fractional distillation of the mixture under reduced pressure. The reaction of *N*-(2-cyanoethyl)dodecylamine with formic

acid and formaldehyde yielded *N*-(2-cyanoethyl)-*N*-methyl-dodecylamine.<sup>4)</sup> Its pyrolysis at 250–270°C and 450 mmHg (1 mmHg ≈ 133.322 Pa) followed by distillation under reduced pressure gave *N*-methyl-dodecylamine. As the second step the amine was neutralized by hydrochloric acid and the salt was purified by repeated recrystallization from ethanol-ethyl acetate mixture.

To obtain dodecyl-dimethylammonium chloride, *N,N*-dimethyl-dodecylamine was prepared as the first step as follows;<sup>4)</sup> formic acid, ethanol solution of dodecylamine, and formaldehyde were mixed and, after reflux for 15 hours, neutralized by 25% aqueous sodium hydroxide solution, *N,N*-dimethyl-dodecylamine being separated as the upper phase. The amine was dried over sodium hydroxide and then distilled under reduced pressure. Dodecyl-dimethylammonium chloride was obtained by the reaction of the amine with hydrochloric acid and recrystallized from benzene-ethyl acetate mixture and then from ethanol-ethyl acetate mixture for five times. The purity of surfactants was confirmed by observing no minimum on the surface tension vs. concentration curves.

Water was distilled three times from alkaline permanganate solution. The surface tension was measured by the drop volume apparatus and procedure described previously,<sup>5)</sup> and the experimental error was within 0.05 mN m<sup>-1</sup>.

### Results and Discussion

The surface tension  $\gamma$  was measured as a function of temperature  $T$  at constant molalities  $m_1$  of the surfactant under atmospheric pressure. The surface tension value of the aqueous solution of DMAC is plotted against temperature in Fig. 1. Figure 2 shows the  $\gamma$  vs.  $m_1$  curves depicted by taking up the  $\gamma$  values in Fig. 1 at a given temperature. It is seen that the curve has a sharp break point, of which the concentration is referred to as a critical micelle concentration (cmc). Looking at Fig. 1, it is observed that the  $\gamma$  vs.  $T$  curve has a minimum at a concentration between about 5 mmol kg<sup>-1</sup> and the cmc, while it is a straight line with a slightly positive slope at a concentration above the cmc. Since the shape of  $\gamma$  vs.  $m_1$  curve changes abruptly at the cmc, the  $\gamma$  vs.  $T$  curve has a break point as indicated by an arrow. For the aqueous DDAC

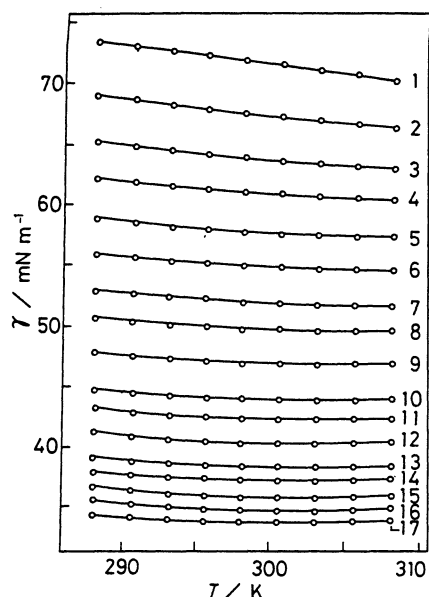


Fig. 1a. Surface tension vs. temperature curves of DMAC at constant concentration under atmospheric pressure: (1)  $m_1=0$  mmol kg<sup>-1</sup>; (2) 1.47; (3) 2.27; (4) 3.03; (5) 3.83; (6) 4.86; (7) 5.66; (8) 6.37; (9) 7.40; (10) 8.74; (11) 9.43; (12) 10.56; (13) 11.67; (14) 12.39; (15) 13.19; (16) 13.87; (17) 14.76.

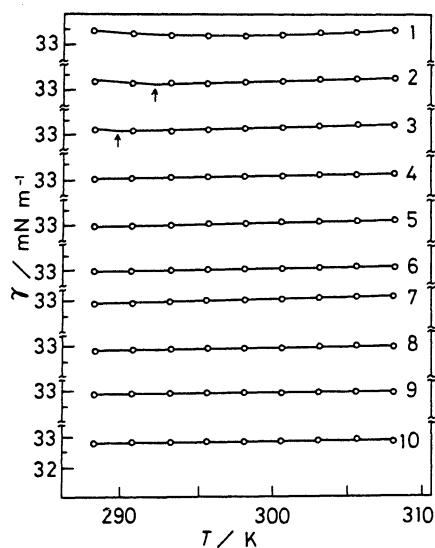


Fig. 1b. Surface tension vs. temperature curves of DMAC at constant concentration under atmospheric pressure: (1)  $m_1=14.94$  mmol kg<sup>-1</sup>; (2) 15.18; (3) 15.56; (4) 16.52; (5) 17.58; (6) 18.69; (7) 21.19; (8) 23.36; (9) 26.29; (10) 36.84.

solution/air interface, similar measurements were made; the  $\gamma$  vs.  $T$  curves at constant molalities and the  $\gamma$  vs.  $m_1$  curves at constant temperatures are drawn in Figs. 3 and 2, respectively. Comparing the curves in Fig. 3 with those in Fig. 1, we notice that the  $\gamma$  vs.  $T$  curve of DDAC has no minimum at a concentration below the cmc and its slope remains negative at a concentration above the cmc.

In Figs. 4 and 5, respectively, the critical micelle concentration vs. temperature curves and the surface

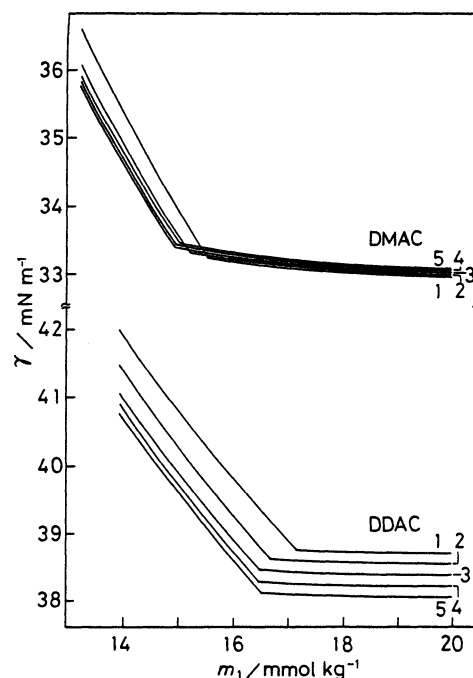


Fig. 2. Surface tension vs. concentration curves at constant temperature under atmospheric pressure: (1)  $T=288.15$  K; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15.

tension vs. concentration curves at 298.15 K of the aqueous solutions of DMAC and DDAC are shown with the corresponding curves of DAC and DTAC. It is seen that the temperature dependence of the cmc value is remarkably large and has a minimum. It is also seen that the cmc and its surface tension  $\gamma^{cmc}$  are correlated to the chemical structure of the polar head-group of surfactant; the *N*-methylation of dodecylammonium chloride successively raises the cmc and

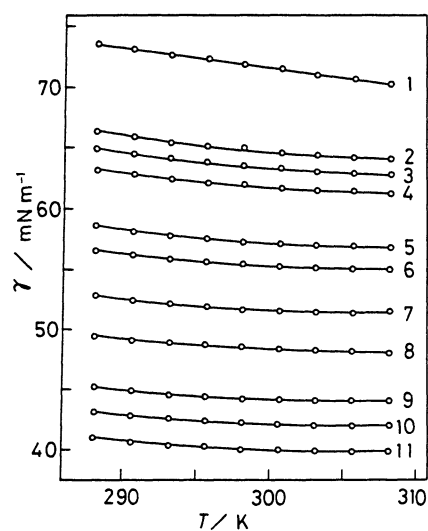


Fig. 3a. Surface tension vs. temperature curves of DDAC at constant concentration under atmospheric pressure: (1)  $m_1=0$  mmol kg<sup>-1</sup>; (2) 2.21; (3) 2.59; (4) 2.93; (5) 4.44; (6) 5.34; (7) 6.90; (8) 8.61; (9) 11.25; (10) 12.98; (11) 15.59.

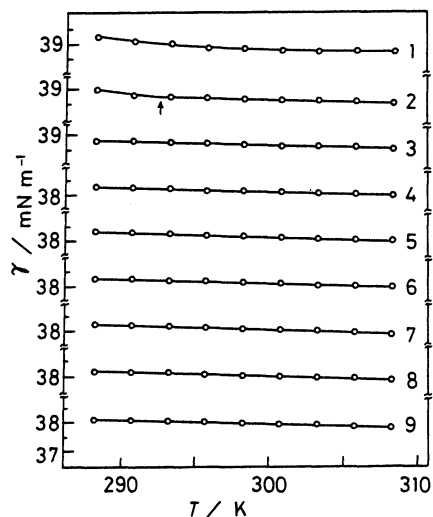


Fig. 3b. Surface tension vs. temperature curves of DDAC at constant concentration under atmospheric pressure: (1)  $m_1=16.17 \text{ mmol kg}^{-1}$ ; (2) 16.76; (3) 17.36; (4) 17.66; (5) 18.43; (6) 22.65; (7) 25.22; (8) 27.95; (9) 38.98.

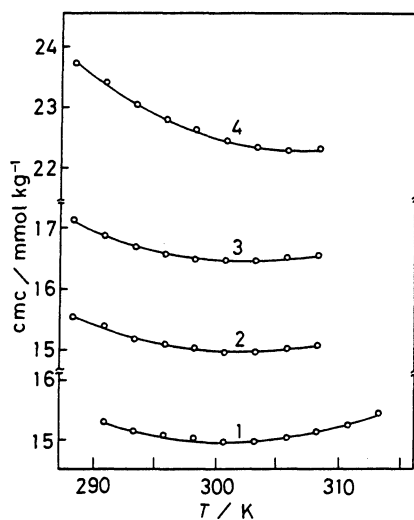


Fig. 4. Critical micelle concentration vs. temperature curves under atmospheric pressure: (1) DAC; (2) DMAC; (3) DDAC; (4) DTAC.

$\gamma^{\text{cmc}}$  values and the differences in the cmc and the  $\gamma^{\text{cmc}}$  values seem to be remarkable between dodecyldimethylammonium chloride and dodecyltrimethylammonium chloride. Such a behavior was also observed in the case of the electric conductivity measurements of the surfactants.<sup>6)</sup>

It has been shown that the derivative of surface tension with respect to temperature is the one of the useful quantities to elucidate the adsorption from the micellar solution.<sup>1,2,5,7-9)</sup> The  $-\partial\gamma/\partial T$  values obtained from Figs. 1 and 3 are shown as functions of molality at constant temperature in Fig. 6. At concentrations below the cmc, they decrease with increasing concentration and raising temperature. At concentrations above the cmc, however, they seem to be almost con-

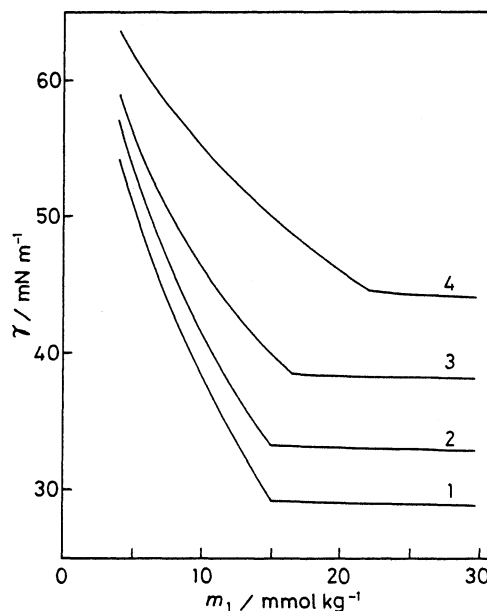


Fig. 5. Surface tension vs. concentration curves at 298.15 K under atmospheric pressure: (1) DAC; (2) DMAC; (3) DDAC; (4) DTAC.

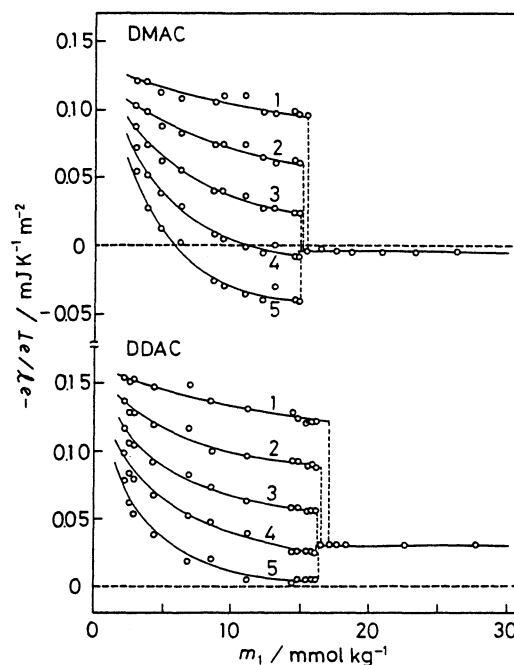


Fig. 6. Derivative of surface tension with respect to temperature vs. concentration curves at constant temperature under atmospheric pressure: (1)  $T=288.15 \text{ K}$ ; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15.

stant. It should be noted that the  $-\partial\gamma/\partial T$  vs.  $m_1$  curves change discontinuously at the cmc.

Now we proceed to analyze the above results with the aid of the thermodynamics of the adsorption of surfactant from its micellar solution.<sup>1)</sup> The adsorbed film is described by the excess thermodynamic quantities with reference to the two dividing plane surfaces

which make the excess numbers of moles of water and air zero. Defining as the thermodynamic quantities of the micelle particle the excess ones with reference to the dividing spherical surface which makes the excess number of moles of water zero, the micelle formation has been shown to be satisfactorily treated as if a new macroscopic phase appears in the solution. At a concentration below the cmc, the entropy change associated with the adsorption of surfactant from the monomeric state in the aqueous solution  $\Delta s(1)$  defined by

$$\Delta s(1) = \Gamma_1^H (s^H / \Gamma_1^H - s_1) \quad (1)$$

is evaluated by the derivative of surface tension with respect to temperature;

$$\Delta s(1) = -(\partial \gamma / \partial T)_{p, m_1}, m_1 < \text{cmc}. \quad (2)$$

Here  $\Gamma_1^H$  and  $s^H$  are respectively the surface excess number of moles of surfactant and surface excess entropy per unit area and  $s_1$  is the partial molar entropy of monomeric surfactant in the aqueous solution. At a concentration above the cmc, the entropy change associated with the adsorption of surfactant from the micellar state  $\Delta s(M)$  defined by

$$\Delta s(M) = \Gamma_1^H (s^H / \Gamma_1^H - s^M / N_1^M) \quad (3)$$

is evaluated by

$$\Delta s(M) = -(\partial \gamma / \partial T)_{p, m_1}, m_1 \geq \text{cmc}, \quad (4)$$

where  $N_1^M$  and  $s^M$  are the excess number of surfactant ions in the micelle and the excess molar entropy of micelle, respectively.

Bearing Eqs. 2 and 4 in mind and looking at the  $-\partial \gamma / \partial T$  vs.  $m_1$  curve in Fig. 6, we may say that the entropy change associated with the adsorption of surfactant from the monomeric state in the aqueous solution is strongly dependent on temperature and concentration, while the corresponding quantity from the micellar state is practically independent of both of them. Similar results have been obtained for the adsorption of DAC and DTAC.<sup>1,2)</sup> It turns out, therefore, that the dependence of the entropy of surfactant on temperature and concentration in the adsorbed film is analogous to that in the micelle though different from that in the aqueous solution.

It is worth noting that the  $\Delta s(M)$  value of DMAC is approximately zero and that of DDAC is obviously positive. Let us consider this point in further detail. Since the surface density of surfactant  $\Gamma_1^H$  usually is a large value at a concentration near the cmc, Eqs. 1 and 3 can be approximated respectively as

$$\Delta s(1) / \Gamma_1^H = \bar{s}_1^H - s_1 \quad (5)$$

and

$$\Delta s(M) / \Gamma_1^H = \bar{s}_1^H - \bar{s}_1^M, \quad (6)$$

where  $\bar{s}_1^H$  and  $\bar{s}_1^M$  are the mean partial molar entropy of surfactant in the adsorbed film and the micelle, respectively.<sup>8)</sup> Using the  $\Gamma_1^H$  vs.  $m_1$  curve obtained by

applying

$$\Gamma_1^H = -(m_1 / 2RT) (\partial \gamma / \partial m_1)_{T, p} \quad (7)$$

to the  $\gamma$  vs.  $m_1$  curve (Fig. 7), we can calculate the left hand sides of Eqs. 5 and 6. The resulting values are given as a function of molality at 298.15 K with those of DAC and DTAC in Fig. 8. It can be seen that the  $\Delta s(M) / \Gamma_1^H$  value varies regularly from a negative one for DAC to a positive one for DTAC with the *N*-methylation of dodecylammonium chloride. Therefore we may say that the *N*-methylation has a different effect on the entropy of surfactant in the adsorbed film from that in the micelle. This view is supported by the fact that the aggregation number of the DAC micelle is

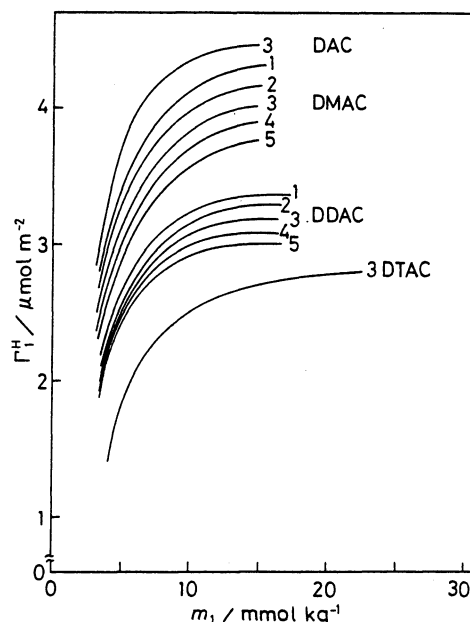


Fig. 7. Surface excess number of moles vs. concentration curves at constant temperature under atmospheric pressure: (1)  $T=288.15$  K; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15.

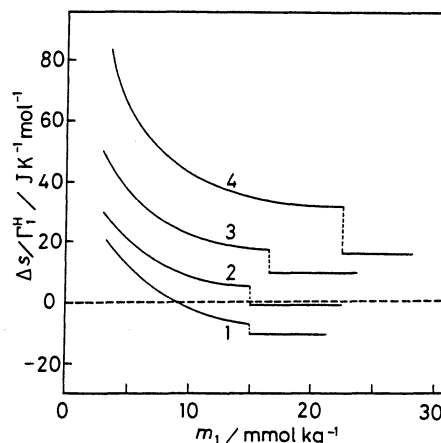


Fig. 8. Entropy change associated with the adsorption per mole of surfactant vs. concentration curves at 298.15 K under atmospheric pressure: (1) DAC; (2) DMAC; (3) DDAC; (4) DTAC.

more than 2 times that of the DTAC micelle at 298.15 K.<sup>10</sup> Figure 8 also shows that the  $\Delta s(1)/\Gamma_1^H$  value of surfactants regularly varies with the *N*-methylation of the head group. Comparing with Fig. 7, it is understandable that the variation of  $\Delta s(1)/\Gamma_1^H$  is primarily correlated to that of the saturated value of  $\Gamma_1^H$  and accordingly to the geometry of the head group.

Let us now consider the abrupt change of the temperature derivative of surface tension seen in Fig. 6. If the micelle formation can be treated like an appearance of a new phase in the aqueous solution, we have

$$[\Delta s(1) - \Delta s(M)]/\Gamma_1^H = -(2RT/\text{cmc})(\partial \text{cmc}/\partial T)_p. \quad (8)$$

In Fig. 9, the value of the left hand side, which was evaluated by using the  $-\partial\gamma/\partial T$  vs.  $m_1$  curve given in Fig. 6 and the  $\Gamma_1^H$  vs.  $m_1$  curve given in Fig. 7, is plotted against temperature by the circle and, on the other hand, the value of the right hand side, which was evaluated from the slope of the cmc vs.  $T$  curve given in Fig. 4, is drawn by the full line. It is seen that the values of both sides are in fair agreement with each other within the experimental error. This finding justifies the validity of our thermodynamic treatment of the micelle formation.

Taking into account Eqs. 5 and 6, we have the relation

$$[\Delta s(1) - \Delta s(M)]/\Gamma_1^H = \bar{s}_1^M - s_1, \quad (9)$$

the right hand side being regarded as the entropy of micelle formation  $\Delta_w^M s$ . It is seen from Fig. 9 that the value  $\Delta_w^M s$  decreases with increasing temperature and becomes negative. Noting that the value of  $\Delta_w^H s$  defined by

$$\Delta_w^H s = \bar{s}_1^H - s_1 \quad (10)$$

also decreases with increasing temperature, we may say that the  $s_1$  value increases remarkably with increasing temperature. Further it is seen that the difference in  $\Delta_w^M s$  between DAC and DTAC is about  $10 \text{ J K}^{-1} \text{ mol}^{-1}$  while that in  $\Delta_w^H s$  is about  $40 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298.15 K. This observation supports the view that the adsorbed film at a plane interface is influenced more significantly by the *N*-methylation of DAC than the spherical micelle.

It is now useful to examine the adsorption of the surfactants from their micellar solutions from the viewpoint of energy. The energy changes associated with adsorption from the monomeric state in the aqueous solution  $\Delta u(1)$  and from the micellar state  $\Delta u(M)$  are evaluated by

$$\Delta u(1) = \gamma + T\Delta s(1) - p\Delta v(1) \quad (11)$$

and

$$\Delta u(M) = \gamma + T\Delta s(M) - p\Delta v(M), \quad (12)$$

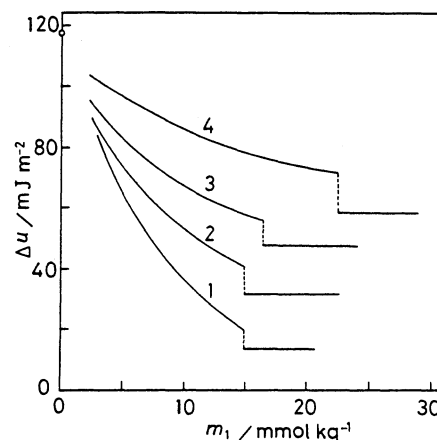


Fig. 10. Energy change associated with the adsorption vs. concentration curves at 298.15 K under atmospheric pressure: (1) DAC; (2) DMAC; (3) DDAC; (4) DTAC.

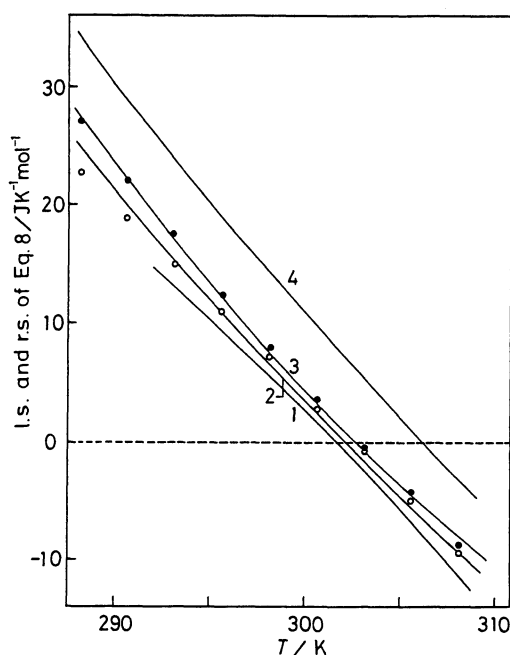


Fig. 9. Comparison between the left and the right side of Eq. 8: (○, ●) left side; (—) right side; (1) DAC; (2) DMAC; (3) DDAC; (4) DTAC.

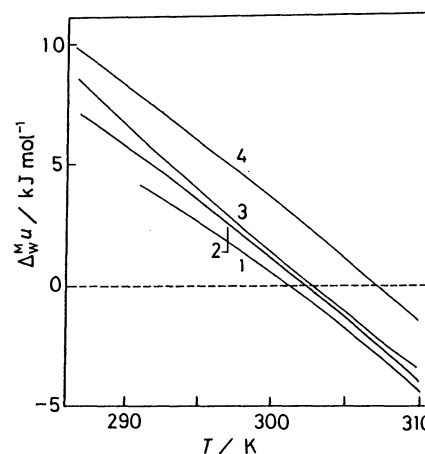


Fig. 11. Energy change of micelle formation vs. temperature curves under atmospheric pressure: (1) DAC; (2) DMAC; (3) DDAC; (4) DTAC.

respectively. Here  $\Delta v(1)$  and  $\Delta v(M)$  are the corresponding volume changes; the  $p\Delta v$  terms are negligibly small compared with the others under atmospheric pressure.<sup>11)</sup> The  $\Delta u(1)$  and  $\Delta u(M)$  values evaluated are shown as functions of concentration at 298.15 K under atmospheric pressure in Fig. 10. The curve appears to behave similarly to the  $\Delta s$  vs.  $m_1$  curve; the  $N$ -methylation of dodecylammonium chloride regularly increases the values of  $\Delta u(1)$  and  $\Delta u(M)$ . This behavior may be explicable by the increase in the hydrophilicity of the head group of surfactant by its successive  $N$ -methylation. On the other hand, energy of micelle formation  $\Delta_w^M u$  defined by

$$\Delta_w^M u = \bar{u}_1^M - u_1, \quad (13)$$

where  $\bar{u}_1^M$  and  $u_1$  are respectively the mean partial molar energy in the micelle and the partial molar energy in the aqueous solution, is evaluated by use of the equation

$$\Delta_w^M u = [\Delta u(1) - \Delta u(M)] / \Gamma_1^H. \quad (14)$$

Its value is depicted in the form of  $\Delta_w^M u$  vs.  $T$  plot in Fig. 11, which bears a striking resemblance to Fig. 9. Therefore we can say that the  $u_1$  value increases remarkably with increasing temperature. In conclusion, it is possible to say that the successive  $N$ -methylation of DAC exercises considerable effect on

the adsorbed film with changes in its surface density, entropy, and energy brought about by changes in the geometry and the hydrophilicity of the polar head group.

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