ARTICLES

Surface Energy of Ionized-Neutral Dodecyldimethylamine Oxide Micelles

Yayoi Terada,*,† Hiroshi Maeda,‡ and Takashi Odagaki†

Departments of Physics and Chemistry, Faculty of Science, Kyushu University, Fukuoka 812-81, Japan

Received: November 1, 1996; In Final Form: February 26, 1997[⊗]

We calculate the surface energy of a micelle consisting of neutral and ionized dodecyldimethylamine oxides (DDAOs) by Monte Carlo simulation based on a lattice model of the micelle. We obtain the dependence of the surface energy on the fraction α_M of ionized DDAO, the concentration C_S, of salt in an aqueous solution and temperature T. We show that the hydrogen bond between DDAOs plays a significant role in determining the properties of micelles. In order to explain experiments, a DDAO molecule on the micelle surface is assumed to support two hydrogen bonds. We show that the continuous chain of the hydrogen bonds will be made on the surface in equilibrium. The surface energy takes its minimum at a specific value $\alpha_M{}^*$ of the concentration of ionized DDAO and $\alpha_M{}^*$ is shown to be an increasing function of C_S and a decreasing function of T.

1. Introduction

Surfactants have been attracting wide interests because of their usefulness in various practical applications. It is known that surfactants dispersed in water assume various structures depending on its concentration, the temperature, pH of the system, and the coexisting salt concentration. In particular, surfactants form micelles when the concentration exceeds a certain critical value (the critical micelle concentration: CMC).[1] A typical surfactant consists of a long hydrophobic part (called the tail part) and a hydrophilic part (called the head part), and the interaction between surfactant tails and water molecules is believed to be mainly responsible for the micelle formation in water.

Dodecyldimethylamine oxide (DDAO) is one of the surfactants with an amine−oxide functional group, which has been utilized in many chemical−technological applications such as lather stabilizers and artificial membranes. A unique property of DDAO is that a neutral DDAO molecule (n-DDAO) can be ionized by a hydrogen ion H^{+},

$$C_{12}H_{25}N(CH_3)_2O + H^+ \rightleftharpoons C_{12}H_{25}N^+(CH_3)_2OH$$
$$\text{n-DDAO} \qquad\qquad\qquad \text{i-DDAO}$$

and one can control the fraction α_M of ionized DDAO (i-DDAO) of the micelle

$$\alpha_M = \frac{\text{i-DDAO}}{\text{n-DDAO} + \text{i-DDAO}} \qquad (1)$$

by pH. Generally speaking, the ionized molecule has a bulkier head and the Coulombic interaction between two i-DDAO molecules enhances this tendency, and thus the CMC is expected to increase as α_M is increased, that is as pH of the system is reduced. To the contrary of this expectation, Herrmann[2] first showed that the CMC of n-DDAO and i-DDAO do not differ much. Tokiwa and Ohki[3] observed that the dependence of the

---

* To whom correspondence should be addressed: E-mail, tera3scp@mbox.nc.kyushu-u.ac.jp.
† Department of Physics.
‡ Department of Chemistry.
⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

dissociation constant pK_m of i-DDAO on α_M above the CMC is different from that below the CMC, indicating that DDAOs in micelles have an extra mutual interaction. Goddard and Kung[4] measured the surface tension of a monolayer of an amine oxide with a long tail and found that the tension shows a minimum as a function of α_M.

Recent systematic experimental studies[5,6] for dilute DDAO solutions have revealed that the CMC and the surface free energy of the solution depend strongly on α_M and assumes a minimum near $\alpha_M = 0.5$ and that the average aggregation number of micelles assumes a maximum at the same values of α_M. They also found that DDAO micelles are stabilized by a salt added into the solution.

From the theoretical point of view, little is known about the origin of the characteristic behavior of DDAO solutions. Mille[7] proposed to include an attractive interaction between i- and n-DDAOs due to hydrogen bonding besides the hydrophobic interaction and the Coulombic repulsion in order to understand the properties of a mixture of n-DDAO and i-DDAO. In fact, the existence of hydrogen bonds (H-bonds) in the case of high polymers in water has now been known in many systems,[8] although the H-bond between caprylate−caprylic acid has been shown to be quite unstable in aqueous solution.[9] However, the effect of H-bonds is hard to incorporate into a theoretical framework, such as the regular solution approach,[10] since one has to take account of the anisotropic nature of H-bonds.

In this paper, we study the surface energy of a micelle consisting of n-DDAO and i-DDAO by Monte Carlo (MC) simulation and investigate the effects of hydrogen bonding in micelle formation. In section 2, we explain our model system is to be used in the following simulation. We take account of the attractive interaction due to hydrogen bonding via H^{+} ion attached to a DDAO molecule as well as the Coulombic repulsion. We include the possibility that a DDAO molecule can support two H-bonds to neighboring DDAOs. In section 3, we present the result of the simulation. We focus on the surface energy due to the Coulombic repulsion and the hydrogen bonding, taking the surface energy of a n-DDAO micelle as the origin of the scale of energy. In fact, this surface energy

Ionized-Neutral DDAO Micelles

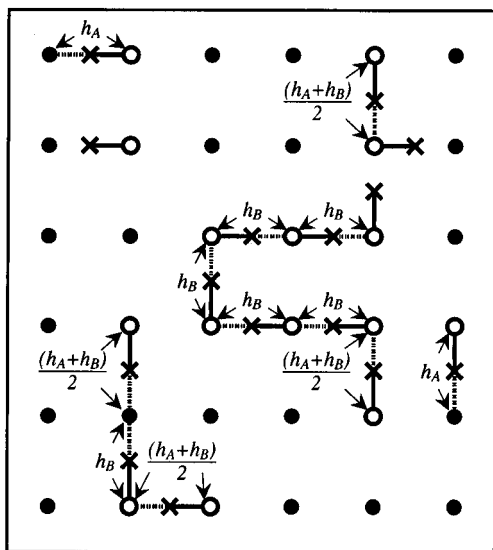*J. Phys. Chem. B, Vol. 101, No. 30, 1997* **5785**

Figure 1. The three different types of H-bonds on the micelle surface: closed circles are the heads of n-DDAO molecules, open circles are the heads of i-DDAO molecules, crosses are H atoms, the solid lines are the chemical bonds, the dashed lines are the hydrogen bonds. The hydrogen bonding energies for the H-bonds of types A, B, and C are taken to be h_A, h_B, and $^1/_2(h_A + h_B)$, respectively.

has been estimated[5] and we can compare our results with experiments.[5,6] We also consider effects of coexisting salts, which reduce the Coulomb energy because of the screening effect, and the temperature dependence of the energy. Section 4 is devoted to summary and discussion of the results.

2. Model

As explained in the Introduction, DDAO molecules form micelles, when the concentration exceeds the CMC. Since our purpose of this study is to investigate effects of H$^+$ ions on the surface, we ignore the curvature of the surface and approximate the surface by a square lattice with periodic boundary conditions. We prepare a 16 × 16 square lattice and assume that the lattice sites are the head of DDAO molecules. (Although tails of molecules are considered to be on one side of the surface, we do not include the tails explicitly in the following discussion.) We initiate our MC simulation by attaching randomly H$^+$ ions to lattice sites with a fixed concentration α_M, where α_M denotes the number of H$^+$ ions per lattice site, which is identical to the concentration of i-DDAO. We assume that an H$^+$ ion ionizes the amine−oxide group and a hydrogen atom (H atom) is located on one of four bonds leaving the site and that there are no H-bonds in the initial stage of MC simulation. In each step of the succeeding MC simulation, we choose randomly an H atom and move it by the standard Metropolis algorithm: If the energy of a final state E_f is lower than or equal to the energy of the initial state E_i, then the final state is taken as the initial state for the next step with probability 1, and if $E_f > E_i$, the probability is reduced to $\exp[(E_i - E_f)/k_BT]$, where T is the temperature and k_B is the Boltzmann constant. As the final state of each MC step, we move the H atom to one of six adjacent bonds and allow it to form or not to form an H-bond. We also allow the H atom to stay on the same bond (attached to the adjacent site or remains on the same site) and to form an H-bond if it has not been formed yet or break the H-bond if it has been already formed one. If it is moved to bonds associated with the neighboring site, we transfer the charge as well. We also take account of the fact that (1) a single bond cannot accommodate more than one H atom and (2) the number of H-bonds formed by a DDAO cannot be more than two.

The surface energy ΔE of a micelle is measured as the difference

$$\Delta E(\alpha_M) = E(\alpha_M) - E(\alpha_M = 0) \tag{2}$$

and is assumed to be given by the energy due to hydrogen bonding E_H, the Coulombic repulsion E_C, and the dipole−dipole interaction between heads of n-DDAO molecules E_D. In our model system, we can identify three different types of H-bond, depending on the number of H-bonds supported by DDAOs at the end of the H-bond as depicted in Figure 1: for type A, both DDAOs support only one H-bond under consideration; for type B, both DDAOs support two H-bonds; for type C, one DDAO supports one H-bond and the other accompanies an H atom (H-bonded or not) beside the H-bond. We assign energies h_A and h_B to the H-bonds of type A and type B, respectively. In order to reduce the number of parameters, we assume that the energy of the H-bond of type C is given by $^1/_2(h_A + h_B)$. Namely E_H is written as

$$E_H = \sum_{\text{type A}} h_A + \sum_{\text{type B}} h_B + \sum_{\text{type C}} {}^1/_2(h_A + h_B) \tag{3}$$

For the Coulombic interaction between i-DDAOs, we employ the screened Coulomb interaction

$$E_C = \sum_{l,m} \Phi(r_{lm}) \tag{4}$$

where the summation is taken all pairs of i-DDAOs and $\Phi(r_{lm})$ is given by

$$\Phi(r_{lm}) = \frac{Ae^2}{r_{lm}} \exp(-\kappa r_{lm}) \tag{5}$$

$$A = \frac{1}{4\pi\epsilon_0\epsilon_e} \frac{\exp(\kappa b)}{1 + \kappa b}$$

$$\kappa^2 = \frac{e^2 \sum_i n_i z_i^2}{4\pi\epsilon_0\epsilon_e k_B T}$$

$$\epsilon_e = 88.15 - 0.414t + 0.131 \times 10^{-2}\, t^2 - 0.046 \times 10^{-4}\, t^3$$

Here r_{lm} is the distance between i-DDAOs on site l and site m, κ^{-1} is the Debye screening length,[11] which is determined by C_S and T, e is the ionic charge of an H$^+$ ion, ϵ_0 is the dielectric constant of vacuum, ϵ_e is the relative dielectric constant of water at temperature T ($t = T - 273.15$), b is the ionic radius of the amine−oxide group, n_i is the average number of ions of species i in unit volume of solution, and z_i is the average number of ions of species i. When the solution contains salt $(A^{z+})_{\nu_+}B^{z-}{}_{\nu_-}$, $\sum_i n_i z_i^2$ in eq 5 is given by

$$\sum_i n_i z_i^2 = (\nu_+ z_+^2 + \nu_- z_-^2)\, C_S N_A$$

Here C_S (mol dm^{-3}) is the concentration of the salt and N_A is the Avogadro number. We assume that the salt in the solution is NaCl in the following discussion, thus $\nu_+ z_+^2 + \nu_- z_-^2 = 2$. For the dipole−dipole interaction between n-DDAOs, we employ the dipole energy,

$$E_D = \frac{1}{4\pi\epsilon_0\epsilon_e} \sum_{i,j} \frac{p_i p_j}{r_{ij}^3} \tag{6}$$

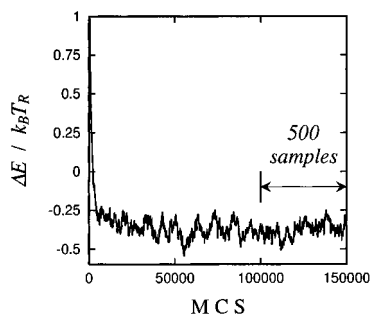where r_{ij} is the distance between n-DDAOs on site i and site j

Figure 2. The typical dependence of the surface energy on the Monte Carlo steps. We judge the equilibrium from the fluctuation of the surface energy. Physical quantities are obtained from 500 samples after 100 000 MC steps ($h_A = h_B = -1.4$ kcal mol^{-1}, $T = 25$ °C, $C_S = 0.30$ mol dm^{-3}, and $\alpha_M = 1.0$).

and p_i is the dipole moment on site i. Here it is assumed that all dipoles are vertical to the surface, and that the dipole moment vanishes when it is ionized by an H$^+$ ion. We continued the MC steps until the system reaches an equilibrium state in which the fluctuation of the energy becomes small compared with the absolute value of the energy, and then we measured the average surface energy and the number of H-bonds as functions of T, α_M, and C_S. Typically, it took 100 000 MC steps to reach the equilibrium state as shown in Figure 2.

3. Results

We first consider properties at room temperature $t = 25$ °C. We have chosen the parameters to simulate the real DDAO–water system as much as possible. Thus we set lattice constant a to the distance between two adjacent DDAOs, $a = 6.5$ Å. The value of energy h_A is estimated to be -1.4 kcal/mol,[6] which is rather small compared to the energy of an isolated H-bond. This is due to the fact that the value we really need for h_A is the difference in energies of an H-bond between a DDAO and water and of an H-bond between two DDAOs. We truncated the summation in $\Phi(r_{lm})$ at $r_{lm} = 46$ Å (seven lattice constant) which is longer than the screening length κ^{-1} ($\kappa^{-1} \cong 22$ Å at $C_S = 0.020$ mol dm^{-3}). We confirmed the results did not change much even when we set the truncation length longer than 46 Å. We have employed 5.0 Debye for the dipole moment p, which is the the largest one among the reported values.[12] We truncated the summation in E_D at $r_{lm} = 6.5$ Å. It turned out that the dipole–dipole interaction between n-DDAO heads does not have much effects on the total surface energy because it is much smaller compared to other two energies, although we have employed the very large value as the dipole moment (When $t = 25$ °C and $r_{ij} = 6.5$ Å, $p^2/(4\pi\epsilon_0\epsilon_e r_{ij}^3) = 0.017$ kcal mol$^{-1} \ll E_C$, $|h_A|$). In the following, we use the value of room temperature $k_B T_R$ as the unit of energy.

3.1. Effects of DDAO Supporting Two H-Bonds. For various values of h_B, C_S, and T, we calculated the surface energy as a function of α_M. Figure 3 shows the Coulombic energy E_C (pluses), the hydrogen-bonding energy E_H (open diamonds), and the total energy ΔE (crosses) per DDAO molecule as functions of α_M for fixed $T/T_R = 1.0$ (room temperature $T_R = 25$ °C), salt concentration ($C_S = 0.20$ mol dm^{-3}) and $h_B/|h_A| = -1.0$. (Namely, the H-bonds of types A, B, and C equally stabilize the system.) The Coulombic energy seems to increase in proportion to α_M^2, because it is determined by the number of i-DDAO pairs occupying nearest-neighbor sites since in this calculation the screening length is comparable to the lattice constant because of large salt concentration C_S ($\kappa^{-1} \cong 6.8$ Å at $C_S = 0.20$ mol dm^{-3}). On the other hand, the hydrogen-bonding energy decreases in proportion to α_M when α_M is small, because
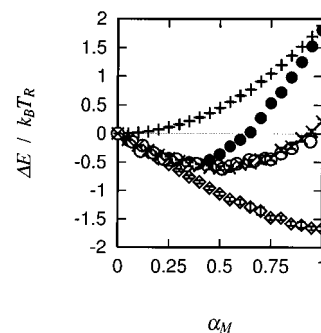
Figure 3. The Coulomb energy(pluses), the hydrogen bonding energies (open diamonds) and the total surface energies (crosses) as a function of α_M when $h_B/|h_A| = -1.0$ ($T = 25$ °C and $C_S = 0.20$ mol dm^{-3}). The total surface energies when $h_B/|h_A| = 100$ is also shown by closed circles. Open circles are experimental data.[5]

an H-bond can be made if an H$^+$ ion exists. When α_M is close to 1, the slope gets so small due to topological constraints that a DDAO cannot support more than two H-bonds. It is clear from this figure that the Coulombic repulsion and the hydrogen bonding give competing contribution to the energy as a function of α_M and that the magnitude of these energies depends on α_M differently. Therefore the total energy shows a minimum at a certain value, α_M^*, of α_M.

The α_M dependence of the free energy of mixed micelle formation, $G_{mic}(\alpha_M)$ at the CMC, has been defined as follows[5]

$$G_{mic}(\alpha_M)/k_B T = \ln \phi_c + (1 - \alpha_M) \ln[(1 - \alpha_1)/(1 - \alpha_M)] + \alpha_M \ln(\alpha_1/\alpha_M) \quad (7)$$

where ϕ_c is the CMC and α_1 is the fraction of i-DDAO monomers in monomeric DDAOs in the system. Assuming that the entropic contributions to $G_{mic}(\alpha_M)$ and to $G_{mic}(\alpha_M = 0)$ are more or less the same, we can compare our surface energy with $\Delta G_{mic}(\alpha_M) \equiv G_{mic}(\alpha_M) - G_{mic}(\alpha_M = 0)$, which is shown by open circles in Figure 3. The agreement between the present results and experiments is satisfactory.

In order to see the effect of DDAOs supporting two H-bonds, we show by closed circles in Figure 3 the total energy when $h_B/|h_A|$ is set to 100 to make the H-bonds of type B be energetically unfavorable. Although the total energy for this case shows a minimum, the over all qualitative behavior does not agree with the experiments. In particular, the total energy near $\alpha_M = 1.0$ is much higher than the experimental value. Moreover, experiments show that the region in while $\Delta E < 0$ in the ΔE versus α_M plot is rather wide and the surface energy for pure i-DDAO ($\alpha_M = 1.0$) at $C_S \cong 0.2$ mol dm^{-3} is the same as that for pure n-DDAO ($\alpha_M = 0.0$). On the other hand, our simulation shows that the width does not change much when h_B is close to 0 and that it is an increasing function of h_B when h_B is close to h_A as shown in Figure 4, and $\Delta E(\alpha_M = 0.0) \simeq \Delta E(\alpha_M = 1.0)$ at $C_S \cong 0.22$ mol dm^{-3} is realized when $h_B/|h_A| = -1.0$. Therefore $h_B/|h_A| = -1.0$ seems to be a good choice for the energy for the H-bond of type B. We can thus conclude that a DDAO molecule can support two H-bonds with little difference in energies of the H-bonds of types A and B.

We show in Figure 5 the fraction of the H-bonds of types A, B, and C as functions of α_M when $h_B/|h_A| = -1.0$. From Figure 5, we expect that for $\alpha_M > \alpha_M^*$ a significant amount of continuous chain of the H-bonds of type B exist. We show that a typical configuration of H-bonds in the system in Figure 6. In Figure 7 the fractions of DDAO molecules which support zero, one, and two are plotted against α_M.

3.2. Effects of Coexisting Salt and Temperature. We calculated the surface energy for various C_S which are shown

Ionized-Neutral DDAO Micelles

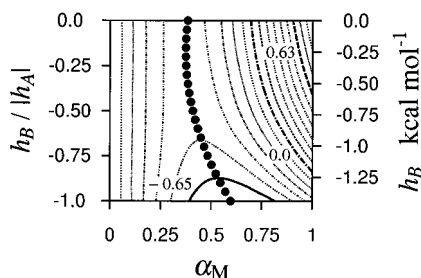*J. Phys. Chem. B, Vol. 101, No. 30, 1997* **5787**

Figure 4. The total surface energy contour on the $h_B/|h_A| - \alpha_M$ domain. The broken line is 0.63, the dot-dash line is 0.0, the solid line is -0.65, and closed circles denote α_M*. The total surface energies show a minimum at α_M* ($T = 25$ °C and $C_S = 0.30$ mol dm^{-3}).
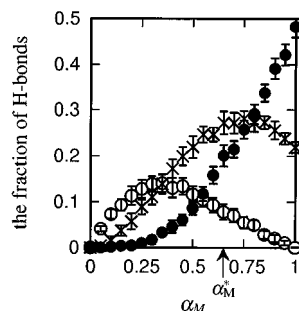
Figure 5. The fraction of the H-bonds of types A, B, and C as functions of when α_M when $h_B/|h_A| = -1.0$. Open circles are the H-bonds of type A, closed circles are the H-bonds of type B, and crosses are the H-bonds of type C ($T = 25$ °C, $C_S = 0.30$ mol dm^{-3}, $\alpha_M* = 0.65$).
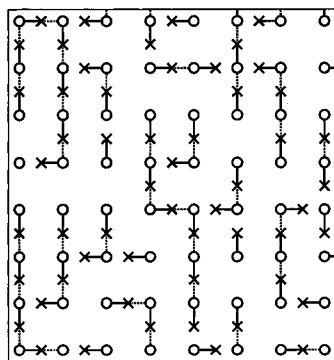
Figure 6. A typical situation of the micelle surface where the continuous chains of the H-bonds of type B are seen. Open circles are the heads of i-DDAO molecules, crosses are hydrogen atoms, the solid lines are the chemical bonds, and the dashed lines are the hydrogen bonds ($h_A = h_B = -1.4$ kcal mol^{-1}, $T = 25$ °C, $C_S = 0.30$ mol dm^{-3}, and $\alpha_M = 1.0$)

as the constant energy contour on the $C_S-\alpha_M$ plane in Figure 8a. The total surface energy decreases as C_S is increased. We can clearly see from this figure that the coexisting salt stabilizes the micelle. This is due to the increase of the screening effect which reduces the Coulombic repulsion. Figures 8b,c show α_M* versus C_S and $\Delta E(\alpha_M*)$ versus C_S, respectively. In order to compare our result with experiments, the experimental data are also plotted in Figures 8b,c. The agreement between the present results and experiments seems to become better for large salt concentration.

In Figure 9 we plot $\Delta E(\alpha_M = 1.0)$ against C_S. We find that, when C_S is above a critical value $C_S* \cong 0.22$ mol dm^{-3}, pure i-DDAO solution ($\alpha_M = 1.0$) is more stable than pure n-DDAO solution ($\alpha_M = 0.0$). This agrees with available experimental results.[5,6] This behavior can well be understood by assuming that a DDAO is possible to support two H-bonds. Figures 10a shows the surface energy contour as a function of T and α_M, and Figures 10b,c show and α_M* and $\Delta E(\alpha_M*)$ as a function
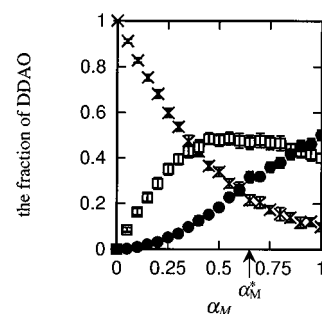

Figure 7. The fraction of DDAO molecules, which support zero (crosses), one (open squares) and two H-bonds (closed circles), as functions of α_M. ($h_A = h_B = -1.4$ kcal mol^{-1}, $T = 25$ °C, $C_S = 0.30$ mol dm^{-3}, and $\alpha_M* = 0.65$)
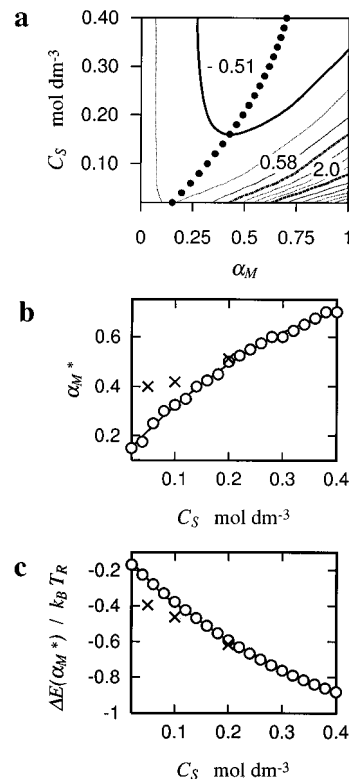

Figure 8. The C_S dependence of the surface energy. (a) The total surface energy contour on $C_S - \alpha_M$ domain: the broken line is 2.0, the dot-dash line is 0.58, the solid line is -0.51, closed circles denote α_M*. The total surface energies show a minimum at α_M*, (b) α_M* as a function of C_S, and (c) $\Delta E(\alpha_M*)$ as a function of C_S ($h_A = h_B = -1.4$ kcal mol^{-1}, $T = 25$ °C). In b and c, open circles are calculated results and crosses are experimental data.[5] The solid line is a guide to eyes.

of T. We find that α_M* is a decreasing function of T and $\Delta E(\alpha_M*)$ is an increasing function of T.

4. Summary and Discussion

We have investigated effects of H-bonds in the micelle formation of n- and i- DDAO in aqueous solution. We showed that the total energy has a minimum as a function of α_M because the Coulombic energy competes with the hydrogen-bonding energy in the ionized-neutral DDAO system. Many ionized-neutral mixed micelles show a minimum in the CMC as a function of the micelle composition because of effects other than hydrogen bonding.[10] In the DDAO system the hydrogen bonding plays a significant role. Comparing our results with experiments for the surface energy of pure n-DDAO and pure i-DDAO, we concluded that the H-bond of type B must be
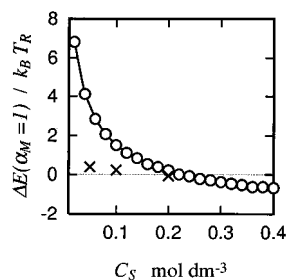
Figure 9. $\Delta E(\alpha_M = 1.0)$ as a function of C_S: open circles are calculated, and crosses are experimental data.[5] When $C_S > C_S^* \cong 0.22$ mol dm^{-3}, pure ionized DDAO solution ($\alpha_M = 1.0$) is more stable than neutral DDAO solution ($\alpha_M = 0.0$). ($h_A = h_B = -1.4$ kcal mol^{-1}, $T = 25$ °C.) The solid line is a guide to eyes.
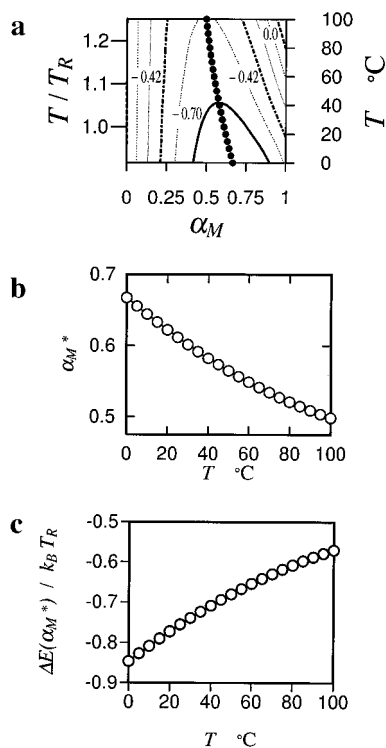

Figure 10. The temperature dependence of surface energy. (a) The total surface energy contour on $T - \alpha_M$ domain; the broken line is 0.0, the dot−dash line is −0.42, the solid line is −0.70, and closed circles are α_M^* as a function of T. The total surface energies show a minimum at α_M^* (b) α_M^* as a function of T, (c) $\Delta E(\alpha_M^*)$ as a function of T ($h_A = h_B = -1.4$ kcal mol^{-1} and $C_S = 0.30$ mol dm^{-3}). The solid lines in b and c is a guide to eyes.

equally possible as the H-bond of type A; namely, a DDAO molecule can support two H-bonds and the second H-bond plays a significant role in determining the properties of micelles. This fact, in turn, indicates that H-bonds will form a chainlike cluster as shown in Figure 6. Concerning the H-bond chains shown in Figure 6, the present model depicted in Figure 1 should be discussed briefly. If one uses the stick and ball model, one can notice that the H-bond chains consisting of more than five

DDAOs are hard to be formed in two dimensions. In Figure 6, long H-bond chains consisting of more than six lattice sites, that is six DDAOs, are seen. This is due to the fact that our lattice model ignores the steric hindrance between the functional groups. The steric hindrance on the actual micelle surfaces seems to be reduced, because the micelle surfaces are curved and not smooth, i.e., the positions of nitrogen atoms need not be confined in a plane but they can be distributed three dimensionally. Therefore, the long H-bond chains seem to be formed even on the actual surface of the micelles as the present model suggests.

We have also studied the effects of coexisting salt and temperature. Our results show that the coexisting salt reduces the surface energy in agreement with experiments. In particular, when $C_S > C_S^*$, pure i-DDAO micelles are more stable than pure n-DDAO micelles because of H-bonds and the strong screening effect of salt. When C_S is small the surface energy of pure i-DDAO micelles in Figure 9 is much larger than the experimental results. This may be due to the fact that we do not include the effect of the counter ions and the Coulombic energy becomes too large when the screening length is large. We also expect the critical value α_M^* decreases as the temperature is increased, which can be tested by experiment because the effect of temperature on the hydrophobic interaction does not have much effect on the dependence of the stability.

It is interesting to note that since the surface energy takes the minimum at α_M^* the micelle near is α_M^* is supposed to be stabilized by H-bonds, and this in turn will reduce the CMC. In fact, experiments show a minimum of the CMC near α_M^*.

References and Notes

(1) Small, D. M. *The Physical Chemistry of Lipids: From Alkanes to Phospholids*; Hanahan, D. J., Ed.; Handbook of Lipid Research 4; Plenum Press: New York, 1986; Chapter 12. Gompper, G.; Schik, M. *Self-Assembling Amphiphilic Systems*; Domb, C., Lebowitz, J. C., Eds.; Phase Transitions and Critical Phenomena 16; Academic Press: London, 1994; Chapter 1.

(2) Herrmann, K. W. *J. Phys. Chem.* **1962**, *66*, 295.

(3) Tokiwa, F.; Ohki, K. *J. Phys. Chem.* **1966**, *70*, 3437. *J. Colloid Interface Sci.* **1968**, *27*, 247.

(4) Goddard, E. D.; Kung, H. C. *J. Colloid Interface Sci.* **1973**, *43*, 511.

(5) Kaimoto, H.; Shoho, K.; Sasaki, S.; Maeda, H. *J. Phys. Chem.* **1994**, *98*, 10243. Maeda, H.; Muroi, S.; Ishii, M.; Kaimoto, H.; Nakahara, T.; Motomura, K. *J. Colloid Interface Sci.* **1995**, *175*, 497.

(6) Maeda, H. *Colloids Surf. A* **1996**, *109*, 263.

(7) Mille, M. *J. Colloid Interface Sci.* **1980**, *81*, 169.

(8) Kawaguchi, S.; Kitano, T.; Ito, K. *Macromolecules* **1991**, *24*, 6030. *Ibid.* **1992**, *25*, 1294.

(9) Friberg, S. E.; Mandell, L.; Ekwall, P. *Kolloid Z.u.Z. Polym.* **1969**, *223*, 955.

(10) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984.

(11) Moore, W. J. *Physical Chemistry*, 4th ed.; Prentice-Hall, Inc: New Jersey, 1972; Chapter 10, Section 23.

(12) Linton, E. P. *J. Am. Chem. Soc.* **1940**, *62*, 1945.