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# Structure of Lyotropic Liquid Crystals of the Dodecyldimethylamine Oxide–HCl–Water System

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Lyotropic phase behaviors of the nonionic and cationic (protonated) forms of dodecyldimethylamine oxide (DDAO) were investigated. Phase diagrams for DDAO + water, hydrochloric acid salt of dodecyldimethylamine oxide (DDAOHCl) + water, and an equimolar mixture of DDAO and DDAOHCl (DDAO(1/2)HCl) + water systems were determined on the basis of polarized light microscopy, small-angle X-ray diffraction, and differential scanning calorimetry. Also, water activity was measured to see the nonideality of water in lyotropic liquid crystalline phases. From the analysis of the composition dependence of the hexagonal unit-cell parameter, the anisometry of the cylindrical micelles in the hexagonal phase,  $\mu (=l/2R_{hc})$ , where  $l$  and  $R_{hc}$  are length and radius of cylinder, respectively, was estimated. It was confirmed that DDAOHCl and DDAO(1/2)HCl form infinitely long cylinder micelles, whereas DDAO micelles seem short. The characteristics of DDAO(1/2)HCl and DDAOHCl were interpreted in terms of hydrogen bond formation between nonionic and cationic (or two cationic) species. It was suggested that these micelles grow with concentration in the isotropic solution phase domain leading to the transition to hexagonal phase with very long cylindrical micelles.

## Introduction

Surfactants having amine oxide as a hydrophilic head-group may exist in aqueous medium in either nonionic or cationic (protonated) form, and the surfactant-related properties, e.g., critical micelle concentration, aggregation number of micelles, surface excess at air–water interface, and so on, can vary considerably with pH. It was shown actually that the aggregation number of dodecyldimethylamine oxide (DDAO) reached the maximum in the pH region where the degree of ionization became ca. 0.5.<sup>1–5</sup> The characteristics of DDAO have been interpreted in terms of the assumed hydrogen bond between nonionic and cationic species.<sup>1,4–7</sup> It is also suggested that the hydrogen bond is formed between two cationic species as well with the same or a weaker strength.<sup>7</sup>

These works mentioned above were carried out at rather low surfactant concentrations, and studies concerning lyotropic liquid crystalline phases at higher concentrations were scarce.<sup>8</sup> The structure of liquid crystals and the phase behavior of surfactant–water systems are strongly influenced by the interactions between headgroups. One can expect to obtain relevant information about the assumed hydrogen bond between nonionic–cationic and/

or cationic–cationic species by examining the lyotropic phase behavior of the nonionic and cationic (protonated) forms of DDAO in the concentrated region. In this study, phase diagrams for DDAO + water, hydrochloric acid salt of dodecyldimethylamine oxide (DDAOHCl) + water, and an equimolar mixture of DDAO and DDAOHCl + water systems were constructed and compared with one another. We employed polarized light microscopy, small-angle X-ray diffraction, and differential scanning calorimetry (DSC) for the acquisition of phase information. Furthermore, the dependence of water activity on composition was also measured to see the nonidealities of water in lyotropic liquid crystalline phases.

In the liquid crystalline phases of aqueous surfactant systems, composition dependence of the X-ray long spacing provides useful information concerning the structure of the hexagonal phase (denoted as H). The structure of the lyotropic hexagonal phase of surfactant–water systems has been assumed to consist of infinitely long cylinder micelles with a two-dimensional hexagonal order in the plane perpendicular to the cylinder axes. However, recent X-ray experimental results on the sodium dodecyl sulfate (SDS)–water system suggested that the intermicellar distances uniformly decrease in all three dimensions with surfactant concentration and finite-rigid rods are present in the hexagonal phase domain.<sup>9,10</sup> Moreover, evidence for micellar growth with surfactant concentration has been obtained in the hexagonal domain of other surfactant–water systems.<sup>11–13</sup> In this study, a detailed analysis on the X-ray long spacing in the hexagonal domain was performed to decide which model fits better for the H phase of the DDAO–HCl–water system.

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## Experimental Section

**Materials.** Dodecyltrimethylamine oxide (DDAO) was purchased from Aldrich Chemical Co. and used after recrystallized from acetone/ethyl ether mixture and dried in vacuo. Hydrochloric acid salt of dodecyltrimethylamine oxide (dodecyltrimethylhydroxylammonium chloride, DDAOHCl) was obtained as follows. About 0.2 g of DDAO was dissolved in 100 cm<sup>3</sup> of acetone, and dry HCl gas was passed through the solution for about 1 h. After the solvent was evaporated, the residual mass was recrystallized twice from acetone/ethyl ether mixture to give colorless needlelike crystals of DDAOHCl and dried in vacuo. Solid compounds with the chemical composition of DDAO(1/2)HCl were prepared by freeze-drying aqueous solutions of DDAO titrated to half-neutralization with HCl. It was found that the crystalline solid of DDAO(1/2)HCl could be obtained by recrystallization from the solution in which equimolar amounts of DDAO and DDAOHCl were dissolved in acetone/ethyl ether mixture. The obtained crystals of DDAO(1/2)HCl were featherlike and exhibited exactly the same DSC curve as the DDAO(1/2)HCl sample obtained by freeze-drying. The featherlike crystalline sample of DDAO(1/2)HCl was used for most of the present experiments.

**Measurements.** A polarizing microscope (BHSP, Olympus) equipped with a heating/cooling stage (FP82HT, Mettler) was used to observe the optical texture of liquid crystals of surfactant–water mixtures.<sup>14</sup> Samples were prepared by weighing out the surfactant and water into glass capillaries of ca. 1 mm inside diameter. The capillaries were flame-sealed, centrifuged, and then heated to 70 °C for 1–7 days to ensure complete mixing before the observation.

The water activity of the surfactant–water mixtures at 25 °C was determined by the isopiestic method.<sup>15,16</sup> Briefly, the surfactant–water mixtures (ca. 20 mg) with various compositions were put in silver pans, which were sealed in a desiccator containing a NaCl or sucrose solution of known relative humidity as a reference solution. After 2–3 days, the desiccator was opened and the pans were weighed. The percentage change in weights was plotted against the initial composition of the mixtures. The composition of the mixture with the same water vapor pressure as the reference solution was estimated by interpolating the plots to the composition where zero weight change should be observed. By repeating the experiment for reference solutions with different relative humidities, the values of water activity for mixtures containing 40–80 wt % surfactant were obtained.

Small-angle X-ray diffraction was measured by a high-resolution small-angle X-ray scattering instrument equipped with a tungsten/silicon multilayer monochromator and a self-rotating anode system.<sup>13</sup> Monochromatic CuK $\alpha$ 1 radiation ( $\lambda = 0.154\ 05$  nm) from a rotating anode (SRAMP18, Mac Science, Tokyo) operated at 45 kV and 350 mA was focused by the Kratky slit and introduced to the sample. The diffracted X-rays were detected by the digital imaging plate (DIP200, Mac Science) over a scattering angle:  $0^\circ < 2\theta < 5.8^\circ$ . Samples were mounted to a cell having a Mylar-film window, and the temperature was controlled by using the thermostated cell holder.

DSC measurement was carried out with a Seiko Instruments DSC120. The surfactant–water mixtures (5–40 mg) in silver pans were heated to 80 °C to anneal the sample before the measurements, and then DSC heating thermograms were recorded at a heating rate of 1–3 °C/min.

Density measurement for micellar solutions was performed using an oscillating U-tube density meter (Anton Paar DMA 60/602).

## Results and Discussion

**Phase Diagrams.** By observation with the naked eye and polarizing light microscope, and the X-ray diffraction patterns of surfactant–water mixtures with various compositions, phase diagrams of DDAO–water, DDAO(1/2)HCl–water, and DDAOHCl–water systems were constructed as seen in Figure 1. (Here, we assumed that DDAO(1/2)HCl may be considered as an independent

chemical component.) The phase diagram of DTACl (dodecyltrimethylammonium chloride)–water system<sup>17</sup> was also indicated for comparison. It is to be noted that the phase diagram of DDAO–water similar to Figure 1A has already been reported by Laughlin,<sup>18</sup> but the phase diagram for hydrochloric acid salt of DDAO has not been published so far to the best of our knowledge. To obtain information on phase behavior in the highly concentrated region (surfactant concentration >75 wt %), DSC measurements were performed for DDAO(1/2)HCl–water and DDAOHCl–water systems (see Figure 2). The thermograms for DDAO(1/2)HCl–water exhibited two isothermal endotherms starting at 46 and 66 °C, both of which had been attributed to polymorphic transformations of dry DDAO(1/2)HCl crystal. The former (latter) endotherm was observed in the surfactant concentration range over ca. 89 wt % (ca. 95 wt %), and the enthalpy changes per DDAO(1/2)HCl linearly decreased with increase of water content. On the basis of these observations, polytropic discontinuities<sup>19</sup> and expected crystal hydrates (denoted as  $S_w$  and  $S_{2w}$ ) were indicated in the phase diagram (see Figure 1B). For the DSC thermograms of dry crystals of DDAOHCl (Figure 2C), on the other hand, the endothermic peak at 80 °C ( $\Delta H = 32.5$  kJ/mol) was related to alkyl chain melting and that at 91 °C ( $\Delta H = 17.2$  kJ/mol) to a solid-to-liquid crystal transition. By addition of a small amount of water, the former peak broadened and shifted to lower temperature, whereas the latter peak disappeared.

Comparing the phase diagrams of DDAO, DDAO(1/2)HCl, and DDAOHCl, one can see that the upper temperature limit of hexagonal phase of DDAO and DDAO(1/2)HCl is ca. 105 °C, but the hexagonal phase of DDAOHCl extends to over 120 °C. Further, the lower temperature limit of the lamellar phase of DDAO and DDAO(1/2)HCl is lower than 20 °C, while that of DDAOHCl is ca. 37 °C. A possible explanation for this may be due to the nonexistence of crystal hydrates for the DDAOHCl–water system. When the lamellar phases are cooled, phase separation occurs to form a more dilute liquid crystal phase and a more concentrated crystal phase. The dilution effect of liquid crystal is more pronounced for DDAOHCl than DDAO or DDAO(1/2)HCl since the coexisting crystal phase is *dry*. This may lead to the lamellar  $\rightarrow$  cubic phase transition at a higher temperature.

It is interesting to compare phase diagrams of DDAOHCl with that of DTACl to see the effects of substitution of hydroxyl group by methyl group. The headgroup structures resemble each other, but the hydroxyl group can form a hydrogen bond whereas the methyl group cannot. One can see that a cubic micellar phase ( $Q_m$ , space group  $Pm\bar{3}n$ ) extends between the hexagonal and the isotropic micellar solution phases in DTACl while a direct isotropic liquid–hexagonal phase transition occurs for DDAOHCl. The reason for this difference between the two will be discussed later. (We may note, in passing, that the effects of *N*-methylation on the phase diagram of dodecylammonium chloride have already been reported.<sup>20</sup>)

**X-ray Diffraction Pattern and Water Activity.** The small-angle X-ray diffraction patterns observed for the liquid crystalline phases of the DDAO–HCl–water system are shown in Figure 3. For the hexagonal phase of

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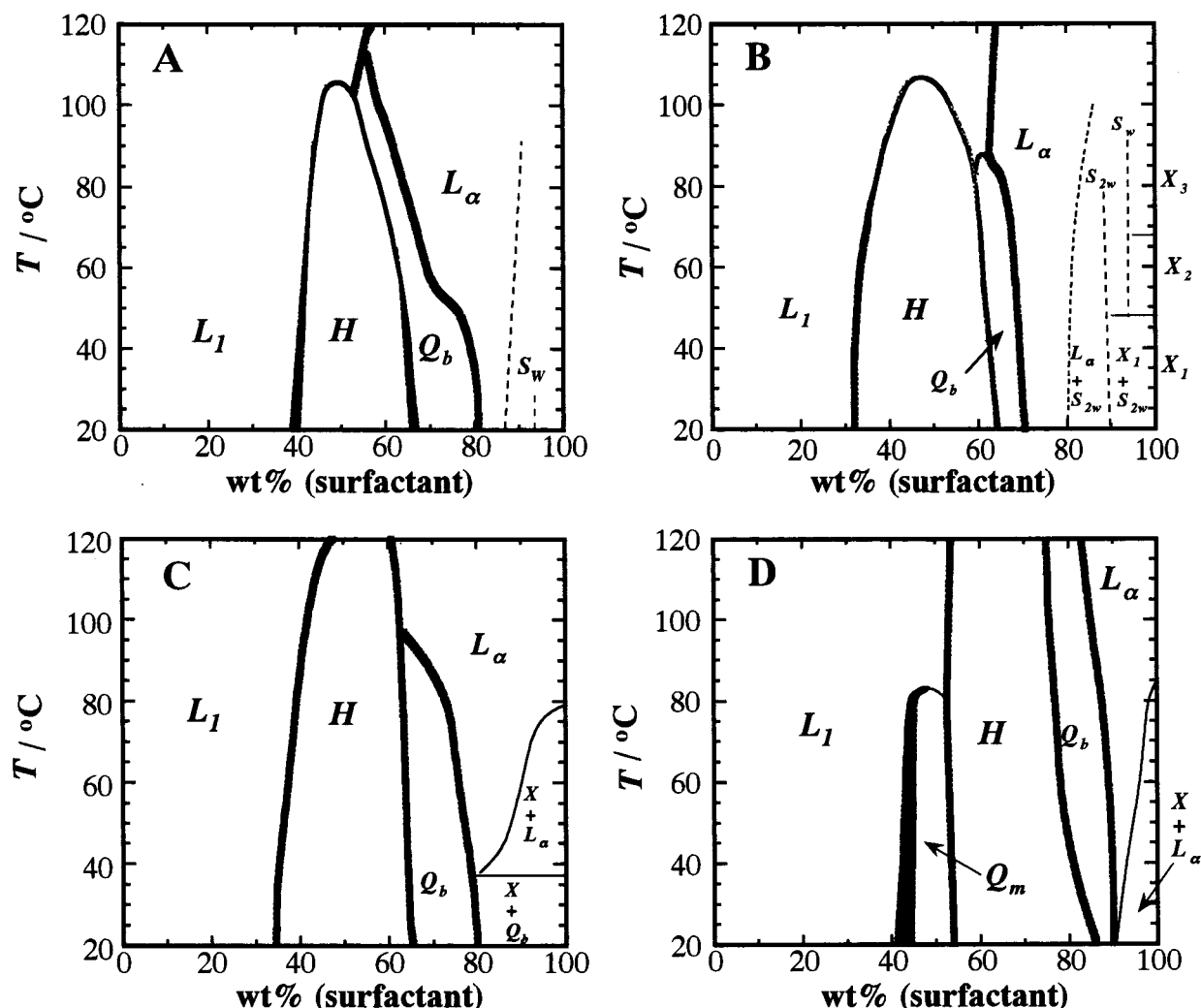
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**Figure 1.** Phase diagram of surfactant–water systems: DDAO–water (A), DDAO(1/2)HCl–water (B), DDAOHCl–water (C), and DTACl–water (D).  $L_1$ ,  $Q_m$ ,  $H$ ,  $Q_b$ , and  $L_a$  indicate isotropic micellar solution, cubic micellar phase, hexagonal phase, bicontinuous cubic phase, and lamellar phase, respectively.  $S$  and  $X$  indicate solid hydrate and dry crystal, respectively. Formation of monohydrate of DDAO,  $S_w$ , was according to Laughlin.<sup>18</sup> Phase diagram of DTACl–water was redrawn from Balmбра et al.<sup>17</sup>

DDAOHCl, the strong diffraction peak for the (10) plane around  $2\theta = 2.2^\circ$  and the minute diffraction from the (12) plane around  $2\theta = 4^\circ$  can be seen. For the hexagonal phase of DDAO and DDAO(1/2)HCl, however, only the diffraction for the (10) plane is confirmed. With the decrease of water content, phase transition from hexagonal to bicontinuous cubic phase (space group  $Iad3$ ) occurs and two diffraction peaks indexed as (211) and (220) are observed for these three systems. When the water content is decreased further, phase transition from cubic to lamellar phase occurs for DDAO and DDAO(1/2)HCl, but in the case of the DDAOHCl–water system, crystals of DDAOHCl separate out and coexist with the cubic phase. So, the diffraction from the (001) plane of solid crystal can be seen for 88 wt % DDAOHCl (see Figure 3C).

Figure 4 shows the concentration dependence of the long-spacing  $d$  calculated from the peak position of diffracted X-rays and the water activity obtained by the isopiestic method. Analysis of the X-ray long spacing will be made in the next subsection. Water activities have not received much attention in recent surfactant science, but they are worthy of considerable attention for they are potentially of considerable value in analysis of the phase behavior of surfactant–water systems.<sup>21</sup> In Figure 5, the water activity was plotted as a function of mole fraction

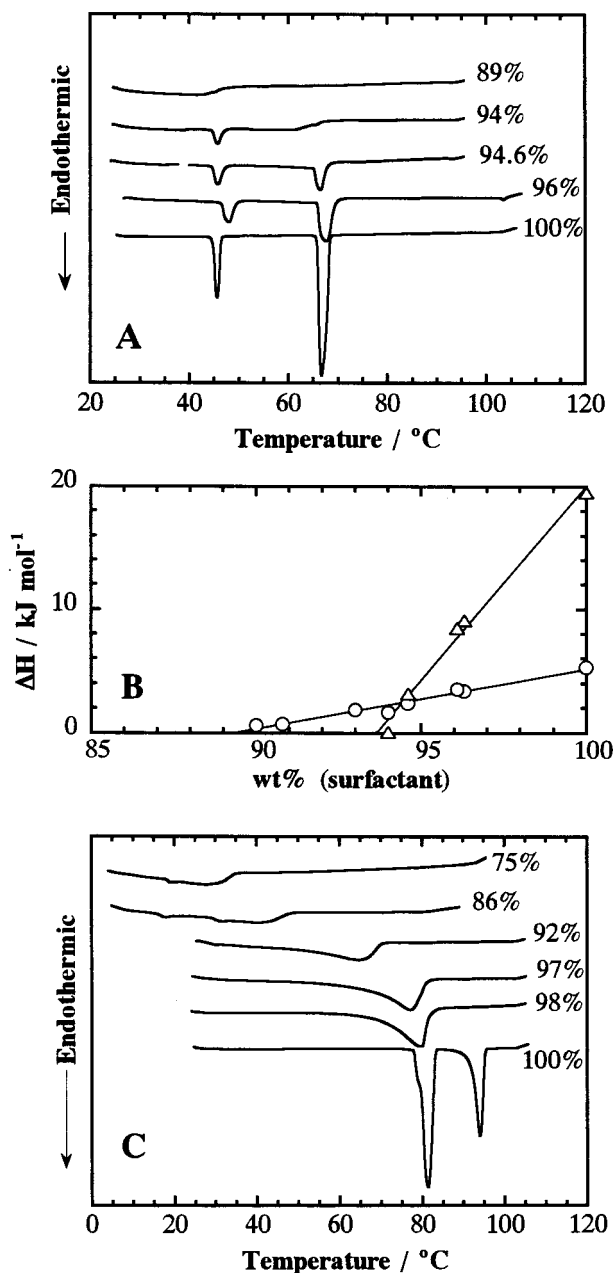
of surfactant,  $X$ . The positive deviation from the Raoult line (which linearly decreases with the surfactant content) is one of the features of the so-called organized solution.<sup>22</sup> When  $0.05 \leq X \leq 0.10$ , where the three systems are all in the hexagonal phase region, water activities for DDAOHCl are slightly lower than those for DDAO(1/2)-HCl and DDAO. In the concentration range  $X \geq 0.11$ , however, water activity for DDAO steeply falls off with concentration, indicating stronger interaction between the nonionic form of DDAO and water than others. This is consistent with the observation that the nonionic species is much more hygroscopic than the other two. Above  $X = 0.22$ , DDAOHCl–water is heterogeneous, i.e.,  $Q_b$  + crystal, and the activity of water becomes constant. At present, we cannot explain the cause of different concentration dependence of water activity for these systems and only mention factors that should be taken into account to analyze the obtained data: the degree of dissociation of  $\text{Cl}^-$  ion, the strength of interaction between water and  $-\text{N}(\text{CH}_3)_2 \rightarrow \text{O}$  (or  $-\text{N}^+(\text{CH}_3)_2\text{OH}$ ) group, and the structural change of liquid crystalline phases with concentration.

**Structure of the Hexagonal Phase.** To inspect the shape of micelles in the hexagonal-phase region, the

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**Figure 2.** DSC heating curves for the DDAO(1/2)HCl–water (A) and DDAOHCl–water systems (C), and composition dependence of specific enthalpy change,  $\Delta H$ , for the endothermic peaks at 47 °C (circle) and at 66 °C (triangle) (B). Weight percent of surfactant is indicated in (A) and (C). Around 190 °C, decomposition of dry crystals of DDAO(1/2)HCl was observed (data not shown). For dry crystals of DDAOHCl, liquid crystal-to-isotropic liquid transition (at 125 °C) and decomposition (at 155 °C) were also observed (data not shown).

hexagonal unit-cell parameter  $a$  ( $=2d/\sqrt{3}$ ) was plotted as a function of volume fraction of surfactant. To estimate the volume fraction, we assumed volume additivity as a first approximation and the following equations were employed

$$\phi = (cv_s)/(cv_s + (1 - c)v_w) \quad (1a)$$

$$\phi_{hc} = (cM_{hc}v_{hc})/(M(cv_s + (1 - c)v_w)) \quad (1b)$$

where  $\phi$  ( $\phi_{hc}$ ) is volume fraction of surfactant (hydrocarbon core),  $v_s$  ( $v_{hc}$ ) is specific volume of surfactant (hydrocarbon core),  $v_w$  is specific volume of water ( $1.003 \text{ cm}^3 \text{ g}^{-1}$ ),  $c$  is

weight fraction of surfactant in the system, and  $M$  ( $M_{hc}$ ) is molecular weight of surfactant (hydrocarbon core), respectively. Since the specific volume of surfactant in hexagonal phase may not differ much from that in micellar solution, the values of  $v_s$  were approximated with the partial specific volumes of micelles, which were calculated using the density data for micellar solutions at 25 °C. The values of  $v_s$  were  $1.109 \text{ cm}^3 \text{ g}^{-1}$  for DDAO,  $1.081 \text{ cm}^3 \text{ g}^{-1}$  for DDAO(1/2)HCl, and  $1.053 \text{ cm}^3 \text{ g}^{-1}$  for DDAOHCl, respectively. For micelles of surfactants with dodecyl chains as a hydrophobic part,  $v_{hc}$  is estimated to be  $1.254 \text{ cm}^3 \text{ g}^{-1}$  and  $M_{hc}$  is 155.30 where one  $\text{CH}_2$  group proximal to the headgroup is not contained within the hydrophobic core.<sup>23</sup> Figure 6 shows the double logarithmic plots of  $a$  vs  $\phi$  ( $\phi_{hc}$ ) for the hexagonal phase of the surfactant–water systems. One can see that linear relation holds for these systems indicating the relation  $a = A\phi_{hc}^{-x} = A'\phi^{-x}$ . The fitting parameters obtained were summarized in Table 1. The exponent  $x$  was estimated to be ca.  $1/2$  for DDAOHCl and DDAO(1/2)HCl, ca.  $1/3$  for DDAO and SDS,<sup>9,10</sup> and 0.12 for DTACL.<sup>12</sup> These results were interpreted according to the analysis of Amaral et al.<sup>9–12</sup> as follows.

As the model for hexagonal phase, let us consider initially a two-dimensional hexagonal array of cylinder micelles with length  $L$  and unit-cell parameter  $a$ , radius of cylinder (hydrocarbon core) of micelles  $R$  ( $R_{hc}$ ), and an average distance  $C$  between micelle centers in the direction of cylinder axis. The volume fractions of cylinder micelles  $\phi$ , and of their hydrocarbon core  $\phi_{hc}$ , must be the same for both the unit cell and the whole system. So<sup>9–12</sup>

$$\frac{L}{C} = \frac{\sqrt{3}}{2\pi} \left( \frac{a}{R_{hc}} \right)^2 \phi_{hc} = \frac{\sqrt{3}}{2\pi} \left( \frac{a}{R} \right)^2 \phi \quad (2)$$

Since this treatment considers a constant density for both hydrocarbon and polar moieties of the micelles as usual,  $R$  and  $R_{hc}$  would be constant irrespective of the composition. If the infinitely long cylinder micelles are formed in the hexagonal phase, then  $L = C$ , and one will get

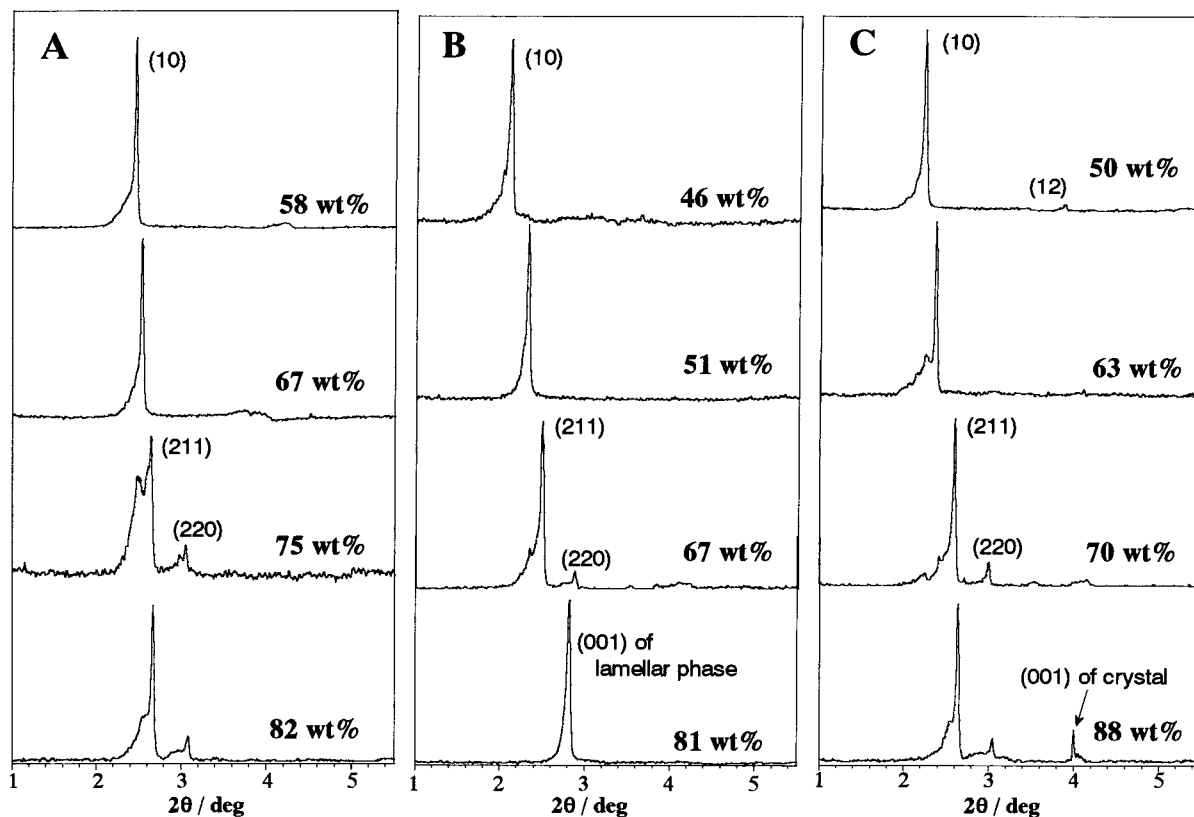
$$a = \left( \frac{2\pi}{\sqrt{3}} \right)^{1/2} R_{hc} \phi_{hc}^{-1/2} = \left( \frac{2\pi}{\sqrt{3}} \right)^{1/2} R \phi^{-1/2} \quad (3)$$

Therefore, we may conclude that the hexagonal phase of DDAOHCl and DDAO(1/2)HCl consists of infinitely long cylinder micelles with a two-dimensional positional order in the plane perpendicular to the cylinder axes. Further, the radius of cylinder micelles,  $R$  and  $R_{hc}$ , can be estimated from the coefficient  $A'$  and  $A$  of the regression curve (see Table 1).

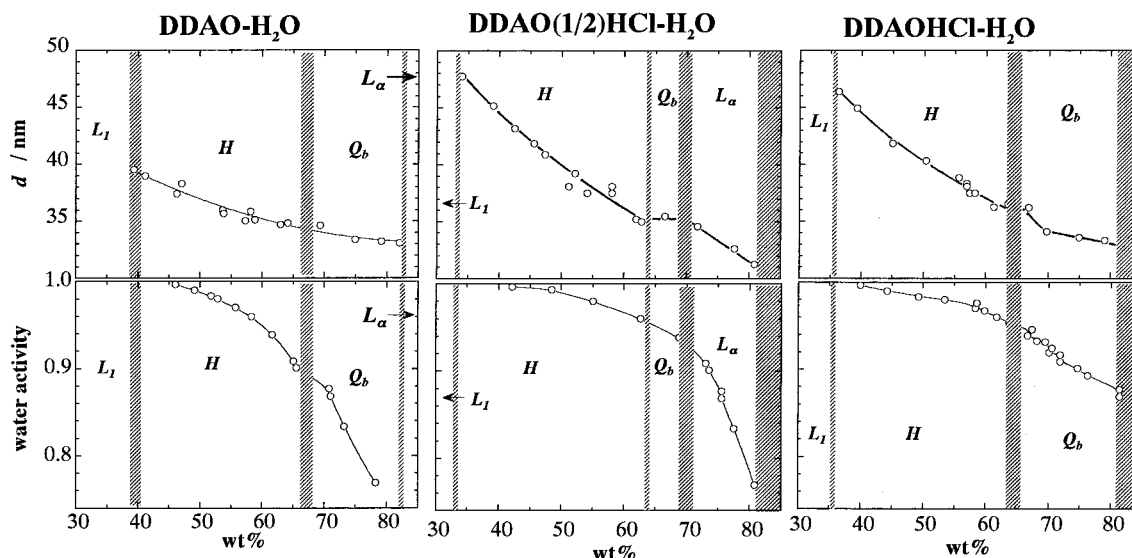
When the exponent  $x$  of the relation  $a \propto \phi_{hc}^{-x}$  is below 0.5 as is the case for DDAO, SDS, and DTACL, an alternative model for hexagonal phase consisting of micelles with finite length should be introduced. As the reasonable shape of micelles with finite length, a spherocylinder with cylinder length  $l$ , radius of hydrocarbon core  $R_{hc}$ , and total length of hydrocarbon core  $L$  ( $=l + 2R_{hc}$ ) is considered as usual. Assuming that interparticle distances decrease uniformly in all three dimension with the decrease of water content, then  $(L/C) = (2R_{hc}/a)$ , and it results<sup>11,12</sup>

$$\frac{L}{C} = \frac{\sqrt{3}}{2\pi} \left( \frac{a}{R_{hc}} \right)^2 \phi_{hc} \left( \frac{1 + \mu}{(2/3) + \mu} \right) \quad (4)$$

where  $\mu = (l/2R_{hc})$  is anisotropy. The anisotropy is



**Figure 3.** Small-angle X-ray scattering patterns for the DDAO-water (A), DDAO(1/2)HCl-water (B), and DDAOHCl-water (C) systems. Weight percent of the surfactant is indicated in the figure. Temperature is 25 °C.



**Figure 4.** Concentration dependence of X-ray long spacing,  $d$ , and water activity for the DDAO-water, DDAO(1/2)HCl-water, and DDAOHCl-water systems. Temperature is 25 °C.  $L_1$ , H,  $Q_b$ , and  $L_a$  indicate isotropic micellar solution, hexagonal phase, bicontinuous cubic phase, and lamellar phase, respectively. Shaded areas denote regions of phase coexistence.

expressed as<sup>11,12</sup>

$$\mu = \frac{K\phi_{hc}^{1-3x} - (2/3)}{1 - K\phi_{hc}^{1-3x}} \quad (5)$$

where  $K = (2\sqrt{3}/\pi)(A/2R_{hc})^3$ . If the condition of uniform decrease in interparticle distance in all three dimensions is fulfilled without the change of micellar shape with concentration,  $x$  should be  $1/3$ , and the anisotropy becomes constant:  $\mu = (K - 2/3)/(1 - K)$ . In contrast, if  $x$  is smaller

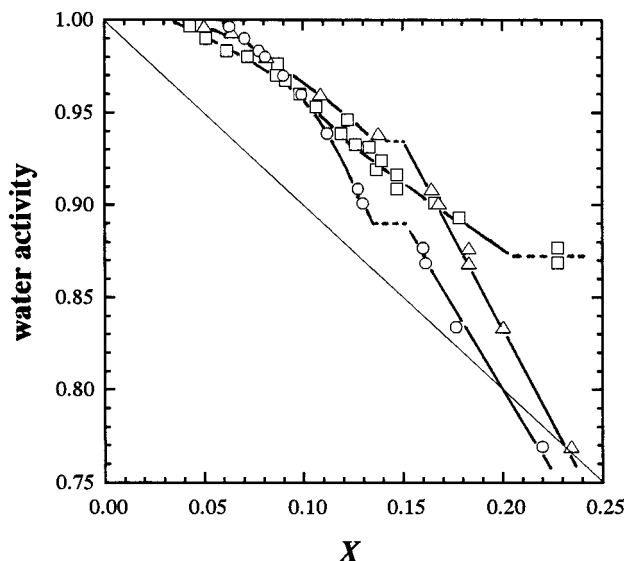
than  $1/3$  as DTACl, eq 5 gives a law for the cylinder growth with concentration since the condition  $1 \geq K\phi_{hc}^{1-3x} \geq 2/3$  corresponds to  $\infty \geq \mu \geq 0$ . Therefore, the analysis of the function  $K\phi_{hc}^{1-3x}$  in the hexagonal domain clarifies the process of micellar growth.<sup>12</sup> In Table 1, the estimated values for  $\mu$  were summarized.

**Micellar Growth and Phase Transition.** We can see in Table 1 that micelles of SDS are finite and have a constant anisotropy in the hexagonal H phase domain. The micellar growth would occur at the isotropic liquid-H phase transition region. For the micelles in isotropic

**Table 1. Fitting Parameters,  $A$  and  $x$ , for the Concentration Dependence of Hexagonal Unit-Cell Parameter  $a$ , and the Estimated Structural Data for Micelles in the Hexagonal Phase**

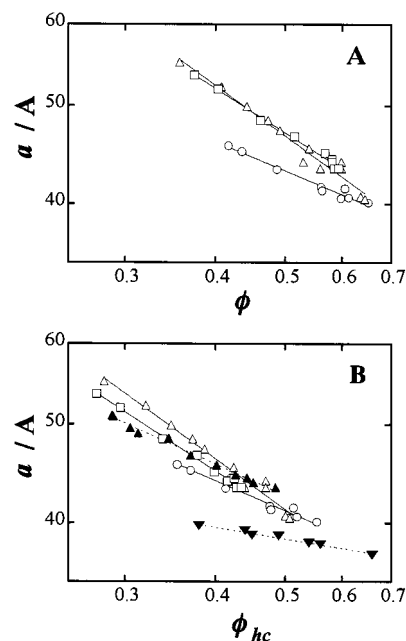
surfactant	$T/^\circ\text{C}$	$A/\text{\AA}$	$x$	$R/\text{\AA}$	$R_{\text{hc}}/\text{\AA}$	$\mu$	ref
SDS	70	33.65	$1/3$		$16.7 \pm 0.1$	6.3	9, 10
DTACl	20	$35.52 \pm 0.14$	$0.118 \pm 0.006$		$15.4 \pm 1.0$	$4.5 - \infty$	12
DDAO	25	$33.1 \pm 0.6$	$0.30 \pm 0.02$		$(17.1)^a$	$(2.3 - 4.7)^a$	this work
DDAO(1/2)HCl	25	$28.9 \pm 0.7$	$0.51 \pm 0.03$	$17.3 \pm 0.4$	$15.1 \pm 0.4$	$\infty$	this work
DDAOHCl	25	$29.4 \pm 0.4$	$0.46 \pm 0.01$	$17.4 \pm 0.2$	$15.4 \pm 0.2$	$\infty$	this work

<sup>a</sup> Tentatively estimated value; see text.



**Figure 5.** Activity of water as a function of mole fraction of surfactant,  $X$ , for DDAO–water (○), DDAO(1/2)HCl–water (△), and DDAOHCl–water (□) at 25 °C. The curves through the points are only guides to the eyes. Raoult line is indicated by the solid line with slope of  $-1$ .

solution of SDS (33 wt %), the estimated spheroid anisometry by X-ray experiments was 2.4.<sup>24,25</sup> In the case of DTACl, on the other hand, the calculated anisometry from eq 5 increases from 4.5 (at  $\phi_{\text{hc}} = 0.40$ ) to infinity with concentration. So, the micellar growth would occur in the H phase domain. For DDAO(1/2)HCl and DDAOHCl, the micelles in H phase can be regarded as infinitely long cylinder and  $\mu$  becomes infinite. The different behavior of  $\mu$  between DTACl and DDAO(1/2)HCl (or DDAOHCl) may be interpreted as follows. The most favored shape of micelles can be adequately described by the geometric packing properties of the surfactant molecules that depend on their optimal headgroup area, the volume of their hydrocarbon chain, and the maximum effective length of their hydrocarbon chain.<sup>26</sup> Because of the hydrogen bond formation between the nonionic and cationic (or two cationic) species, one can regard that the optimal headgroup area for DDAO(1/2)HCl and DDAOHCl becomes smaller than that for DTACl. The surfactants possessing smaller headgroup area are favored to form cylindrical rodlike micelles, and their mean aggregation number is sensitive to the total surfactant concentration. Indeed,



**Figure 6.** Hexagonal parameter,  $a$ , as a function of the volume fraction of surfactant,  $\phi$ , (A) and of the hydrophobic core,  $\phi_{\text{hc}}$ , (B). DDAO–water (○), DDAO(1/2)HCl–water (△), DDAOHCl–water (□), DTACl–water (▼),<sup>12</sup> and SDS–water (▲).<sup>9,10</sup>

the increase of aggregation number with the surfactant concentration has been reported for micelles of ionic surfactants in high salt solution<sup>27–30</sup> and for a typical nonionic surfactant.<sup>31,32</sup> So, we expect that the micellar growth would occur in  $L_1$  domain and then the direct  $L_1$ –H transition occurs for DDAO(1/2)HCl and DDAOHCl. (Some experimental results supporting the idea of the micellar growth in the  $L_1$  domain have been obtained for half-protonated micelles of DDAO.<sup>5</sup>) On the contrary, the micellar growth of DTACl hardly occurs because of the low degree of binding of  $\text{Cl}^-$  to the headgroup<sup>33</sup> resulting in the  $L_1$ – $Q_m$ –H phase sequence. It is to be noted that palmitoyl-lyso-phosphatidylcholine (PLPC)–water system shows the  $L_1$ – $Q_m$ –H phase sequence as well as DTACl–water and PLPC micelles remain with a prolate ellipsoidal shape of constant anisometry in the whole isotropic liquid phase region.<sup>34</sup>

For the micelles of DDAO, we need to know the very accurate value of  $R_{\text{hc}}$  to estimate the anisometry from eq 5. It is to be stressed that the value of  $\mu$  is critically dependent on the  $R_{\text{hc}}$  value adopted, and  $R_{\text{hc}}$  must be greater than 17.1 Å when  $A = 33.1$  Å and  $x = 0.30$  to obtain significant value for  $\mu$ . Assuming  $R_{\text{hc}} = 17.1$  Å,  $\mu$  becomes 2.3 (4.7) when  $\phi_{\text{hc}}$  is 0.35 (0.55), indicating slight

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growth of micelles in the H phase domain. More detailed analysis and exact experimental estimation of  $R_{hc}$  with enough precision<sup>9</sup> will be necessary to confirm the micellar growth behavior of the DDAO–water system.

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