Lower and Upper Consolute Boundaries of Dilute Aqueous Solutions of Dimethyloleylamine Oxide in the Presence of NaCl and HCl. A "Closed Loop" Phase Diagram

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The consolute phase boundaries have been drawn for dilute aqueous NaCl solutions of dimethyloleylamine oxide in the absence and presence of HCl. In the absence of HCl, the LCST is located at 3–19 °C and at surfactant concentrations of $(0.045–0.07) \times 10^{-2}$ g cm^{-3} for NaCl concentrations from 1.0 to 4.0 M. In the presence of 10^{-3} and 10^{-2} N HCl the consolute phase boundaries for aqueous NaCl solutions of surfactant appear at NaCl concentrations higher than 0.047 M at 25 °C. They exhibit a lower consolute NaCl concentration around pH 4.5 or degree of protonation of 0.5. Aqueous 0.05 M NaCl solutions with 10^{-3} N HCl exhibit a "closed loop" profile with the LCST at −13 °C and the UCST at 68 °C. For the occurrence of an LCST on a "closed loop" phase diagram, hydrogen bonding between the micelle particle and water molecules must play an important role in energetically stabilizing rodlike micelles in water at low temperatures. The formation of long rodlike micelles shifts the phase profile toward low temperature and concentration, and makes it very asymmetric.

Introduction

Dimethyloleylamine oxide, CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_8$N(CH$_3$)$_2$O, is a weak base which takes on a nonionic form in neutral and alkaline solutions and is converted to dimethyloleyl-*N*-hydroxyammonium ion by the addition of HCl. According to our light scattering measurements,[1-3] the surfactant molecules in dilute aqueous solutions form micelles above the critical micelle concentration, $(0.003–0.0045) \times 10^{-2}$ g cm^{-3}. Strong scattering intensity or large micelle molecular weight indicates the formation of long and flexible rodlike micelles. The molecular weight or the contour length of rodlike micelles is strongly dependent on the NaCl concentration as well as on the HCl concentration. For concentrated NaCl solutions, liquid–liquid phase separation occurs or strong opalescence is developed, preventing meaningful light scattering measurements.[2,3]

The existence of a region with two isotropic phases has been reported on the phase diagram of dilute aqueous solutions of surfactants by many workers.[4-12] It is known that poly(oxyethylene) alkyl ethers show cloud points as the temperature rises,[10] which are influenced by various additives such as simple salts[13,14] and dyes.[15] The cloud points constitute a lower consolute boundary. Apart from those with polydisperse poly(oxyethylene) alkyl ethers, lower consolute boundaries have been reported for various monodisperse nonionic surfactants in water. A lower critical solution temperature (LCST) was observed for hexa(oxyethylene) alkyl ether, and it was found that the LCST is lower as the alkyl chain is longer.[4] Similar phase diagrams, each composed of two isotropic phases, were observed for the other oligooxyethylene alkyl ethers[6,7,11,12] and dimethyldodecylphosphine

oxide[5] in water.

Besides an LCST, an upper critical solution temperature (UCST) was exhibited by aqueous solutions of dimethyldodecylphosphine oxide at a higher temperature, thus giving a "closed loop" consolute boundary.[9] Dimethyldecylphosphine oxide,[5,9] tetra(oxyethylene) decyl ether,[9] and penta(oxyethylene) decyl ether[9] in water also gave "closed loop" profiles.

In this paper, phase boundaries are drawn for aqueous NaCl solutions of dimethyloleylamine oxide in the absence and presence of HCl. The phase diagram at a fixed HCl concentration is given in the form either of temperature against surfactant concentration at different NaCl concentrations or of NaCl concentration against surfactant concentration at different temperatures. The region of phase separation is discussed in relation to the protonation of the surfactant.

Experimental Section

The sample of dimethyloleylamine oxide, kindly donated by Dr. F. Hoshino of Kao Corporation, Inc., Wakayama, was the same as previously used.[1-3] Guaranteed reagent grade NaCl was ignited before use. Water was redistilled from alkaline KMnO$_4$ in a glass still.

To prepare a solution of desired composition, NaCl and HCl were added to an aqueous solution of surfactant at 25 °C. The concentration of surfactant was varied from 0.005×10^{-2} to 1.1×10^{-2} g cm^{-3}, and the NaCl concentration was changed from 0 to 4.0 M. For measurement of the consolute NaCl concentration for liquid–liquid phase separation, 5 cm^3 of a solution was incubated overnight in a water bath at 25 ± 0.02 °C. The occurrence of phase separation was determined by visual inspection. For the temperature dependence, a solution prepared at 25 °C was sealed in a glass tube of length 15 cm and diameter 1.5 cm and immersed in a Neslab RTE-8 refrigerated water bath at constant temperature. Temperature was varied from 5 to 75 °C with intervals of 5 °C. Examination for phase separation was made after incubation for 4 h, at which time equilibrium had been attained.

The liquid–liquid phase separation produced either a stable emulsion over the whole region or two clearly separated layers. In some cases, the lower of the two layers was homogeneous but the upper one was emulsified. The upper layer was more viscous in all cases. Phases near the critical region were sometimes sensitive to applied shear force. For example, two liquid phases consoluted after shaking.

The potentiometric titration was carried out on an M-225 Iwaki Glass pH/ion meter at room temperature (25 ± 1 °C) under a nitrogen atmosphere. Aqueous solutions of dimethyloleylamine oxide with definite NaCl concentrations were prepared, and their pH was adjusted by adding a standardized HCl or NaOH solution

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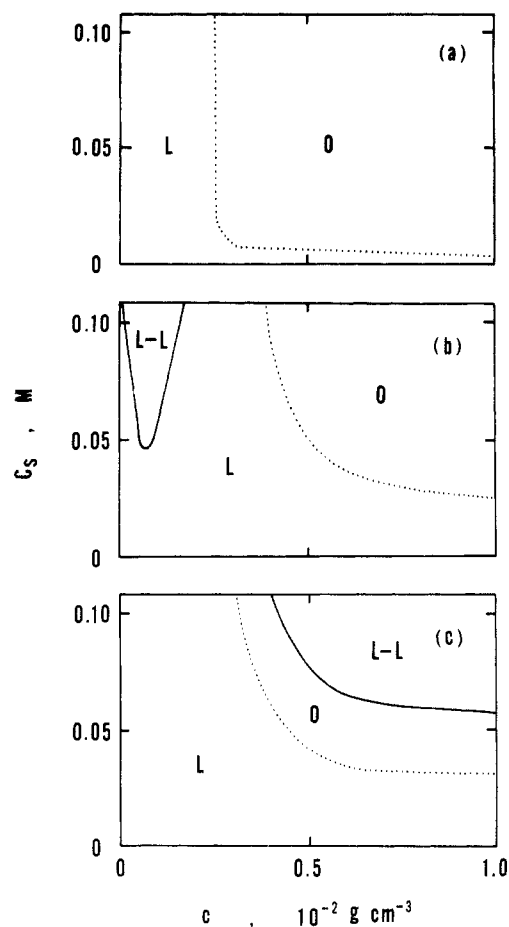(15) Nemoto, Y.; Funahashi, H. *J. Colloid Interface Sci.* **1981**, *80*, 542.
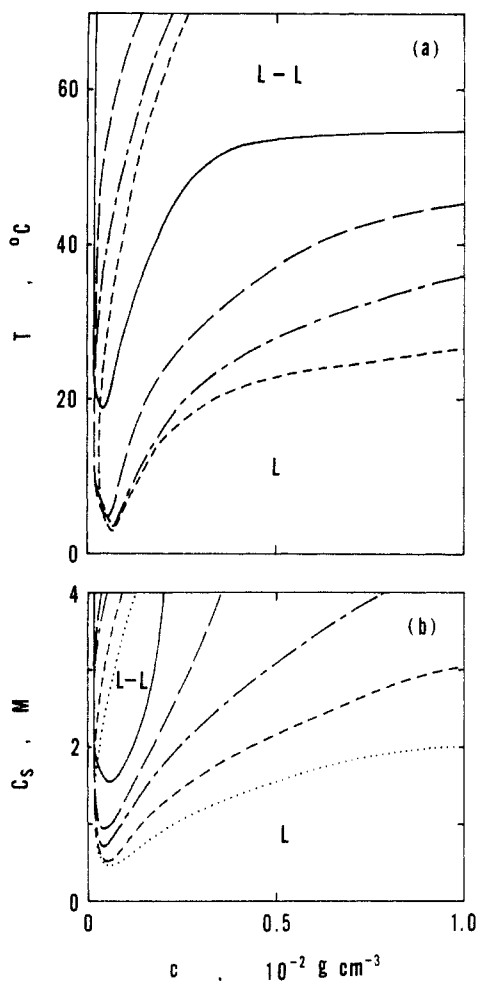
Figure 1. The liquid–liquid phase separation diagram for aqueous NaCl solutions of dimethyloleylamine oxide in the absence of HCl: L, homogeneous region; L–L, two-phase region. (a) NaCl concentration: —, 1.0 M; ––, 2.0 M; –·–, 3.0 M; ---, 4.0 M. (b) Temperature: —, 15 °C; ––, 20 °C; ---, 25 °C; ---, 35 °C; ···, 45 °C.

to a surfactant solution. Each solution was kept overnight before pH measurement, because the pH of the solutions was time dependent but reached equilibrium after a few hours. The degree of protonation of surfactant, α, was calculated by dividing the difference between total and free concentrations of hydrogen ions by the molar concentration of surfactant.

Results

Liquid–Liquid Phase Separation. Figure 1a shows the relationship of temperature for liquid–liquid phase separation vs. surfactant concentration at different NaCl concentrations. While the aqueous NaCl solutions of surfactant are homogeneous at surfactant concentrations below 0.02×10^{-2} g cm^{-3} over the whole temperature range, those of higher surfactant concentrations separate into two liquid phases at high temperatures. The lower consolute temperature generally decreases with an increase in NaCl concentration. The LCST is 19 °C at a surfactant concentration of 0.045×10^{-2} g cm^{-3} for 1.0 M NaCl solution, and it decreases to 3 °C and shifts to 0.07×10^{-2} g cm^{-3} with increasing NaCl concentration up to 4.0 M.

The lower consolute boundary is very asymmetric with respect to the surfactant concentration. It rises very sharply at lower surfactant concentrations, but it rises only gradually at higher surfactant concentrations, especially above 0.5×10^{-2} g cm^{-3}. While the composition of the more dilute phase in 1.0 M NaCl does not change with temperature above 25 °C and remains at 0.02×10^{-2} g cm^{-3}, its composition in solutions with higher NaCl concentrations shifts toward higher surfactant concentrations with a rise of temperature. The upper consolute temperature decreases with a further increase of NaCl concentration above 1.0 M.

Figure 2. The liquid–liquid phase separation diagram at 25 °C for aqueous NaCl solutions of dimethyloleylamine oxide in the presence of different HCl concentrations: L, homogeneous region; L–L, two-phase region; 0, opalescent region. HCl concentration: (a), 0 N; (b), 10^{-3} N; (c) 10^{-2} N.

Figure 1b shows the relationship of NaCl concentration for liquid–liquid phase separation vs. surfactant concentration at constant temperatures, redrawn on the basis of the phase diagram in Figure 1a. The solution at 15 °C separates into two isotropic phases if the surfactant concentration is at $(0.02–0.20) \times 10^{-2}$ g cm^{-3} and the NaCl concentration is higher than 1.5 M. At higher temperatures, phase separation occurs at lower NaCl concentrations but at higher surfactant concentrations. The lower consolute NaCl concentration for phase separation changes quite asymmetrically with the surfactant concentration, rising very sharply at lower surfactant concentrations but more gradually at higher surfactant concentrations.

The addition of HCl brings about a drastic change in the consolute boundary. Figure 2 illustrates the relationship of the consolute NaCl concentration vs. surfactant concentration at 25 °C for solutions with different HCl concentrations. Visual examination further shows that, in addition to liquid–liquid phase separation, opalescence appears above a certain definite surfactant concentration. The dotted line in Figure 2 indicates the threshold for the occurrence of opalescence at the lowest NaCl and the lowest surfactant concentrations. The threshold is quite different from that for liquid–liquid phase separation and has no correlation with it. It looks like a rectangular hyperbola having a vertical asymptote around 0.25×10^{-2} g cm^{-3}. The critical concentration of opalescence would correspond to the overlap micelle concentration above which flexible rodlike micelles begin to superpose. The opalescence could be attributed to the formation of micelle clusters as a result of intermicellar interaction, portending the formation of liquid crystals.

Without added HCl, the surfactant solution remains homogeneous at 25 °C, even if NaCl is added up to 0.7 M. On addition of 10^{-3} N HCl, the surfactant solution separates into two phases
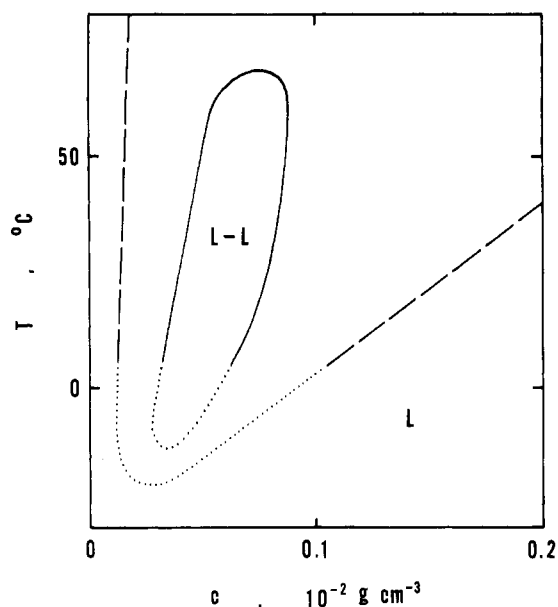
Figure 3. The liquid–liquid phase separation diagram for aqueous NaCl concentration of dimethyloleylamine oxide in the presence of 10^{-3} N HCl: L, homogeneous region; L–L, two-phase region. NaCl concentration: —, 0.05 M; − −, 0.10 M. The dotted part represents the extrapolated curve.
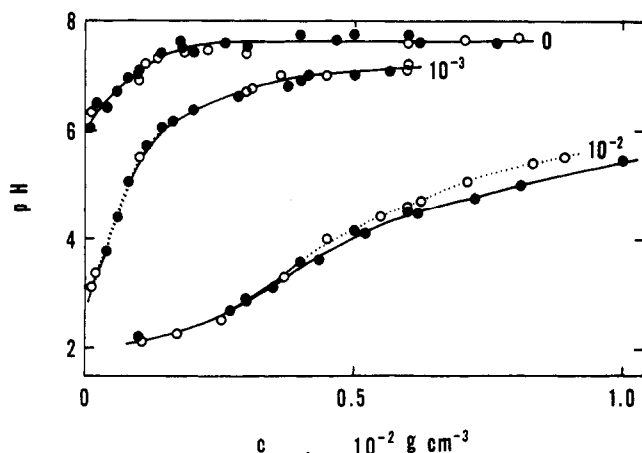

Figure 4. The relationship of pH vs. surfactant concentration for aqueous NaCl solutions of dimethyloleylamine oxide with different HCl concentrations. NaCl concentration: ●, 0.05 M; ○, 0.10 M. The numerical value represents the molar concentration of HCl. The dotted portions indicate the liquid–liquid phase separated region.

at surfactant concentrations of 0.16×10^{-2} g cm^{-3}, if the NaCl concentration is higher than 0.047 M; above and below this surfactant concentration, the NaCl concentration for phase separation sharply rises nearly symmtrically. In the presence of 10^{-2} N HCl, two phases are formed only above 0.057 M NaCl and above 0.4×10^{-2} g cm^{-3} surfactant concentration. It is quite remarkable to see the large difference in phase boundary behavior in the presence of 10^{-3} and 10^{-2} N HCl.

For solutions with 10^{-3} N HCl, the temperature–surfactant concentration relationship for phase separation is shown in Figure 3. In 0.1 M NaCl, phase separation occurs above a surfactant concentration of 0.007×10^{-2} g cm^{-3}, and the LCST is estimated to be –20 °C at 0.025×10^{-2} g cm^{-3} by extrapolation. The phase separation in 0.05 M NaCl occurs in a narrower range of surfactant concentrations at $(0.026–0.088) \times 10^{-2}$ g cm^{-3}, and its diagram forms a "closed loop" with the LCST at –13 °C (by extrapolation) and the UCST at 68 °C.

The pH value of solutions with 0.10 or 0.05 M NaCl and with constant HCl concentration is shown in Figure 4 against the surfactant concentration. The surfactant solutions without HCl exhibit pH values between 6.0 and 7.6, depending on the surfactant concentration. The pH values for 10^{-3} and 10^{-2} N HCl solutions
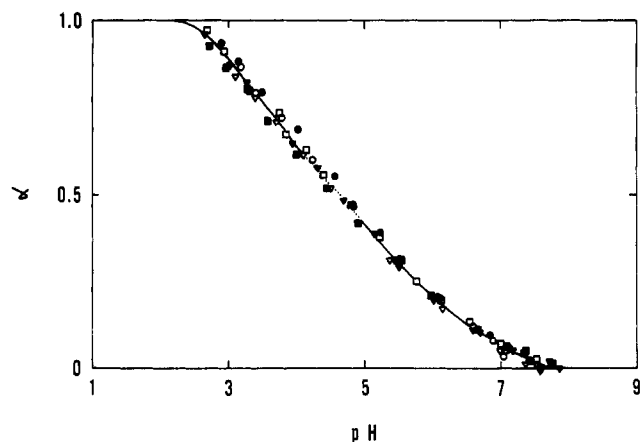

Figure 5. The titration curve for a 0.05 M NaCl solution of dimethyloleylamine oxide at 25 °C. Surfactant concentration (10^{-2} g cm^{-3}): ○, 0.10; ●, 0.20; ▽, 0.30; ▼, 0.40; □, 0.50; ■, 0.60.

of surfactant strongly depend on the surfactant concentration. The dotted portion represents the phase separation region. Phase separation takes place around pH 3.5–6 for 0.10 M NaCl solutions with 10^{-3} and 10^{-2} N HCl and around pH 4–5 for 0.05 M NaCl solutions with 10^{-2} N HCl. Phase separation is strongly dependent on the pH of the solution, as well as on the NaCl concentration.

Potentiometric Titration. A molecule of dimethyloleylamine oxide is nonionic at neutral and alkaline pH but takes on a cationic form as HCl is added, according to the protonation (ionization) equilibrium

$$C_{18}H_{35}N^+(CH_3)_2OH \rightleftharpoons C_{18}H_{35}N(CH_3)_2O + H^+ \quad (1)$$

If α_1 is the degree of protonation of monomer, the dissociation constant of monomer, K_1, is expressed by

$$pK_1 = -\log K_1 = pH + \log\left(\frac{\alpha_1}{1 - \alpha_1}\right) \quad (2)$$

Above the critical micelle concentration, a solution contains monomers and micelles. The apparent degree of protonation, α, observed for a micellar solution is given by an average of the degree of protonation of monomer and micelle as

$$\alpha = \frac{\alpha_1 C_1 + \alpha_m(C - C_1)}{C} \quad (3)$$

where α_m is the degree of protonation of the micelle, C_1 is the molar concentration of monomer, and C is the total molar concentration of surfactant. C_1 can be approximated by the critical micelle concentration, C_0. Then, analogously to polymer solutions,[16,17] the apparent dissociation constant of micelles, $(K_m)_{app}$, is described by

$$(pK_m)_{app} = pH + \log\left(\frac{\alpha_m}{1 - \alpha_m}\right) = pK_m - \frac{0.434}{kT}\frac{\partial G_{el}}{m\,\partial\alpha_m} \quad (4)$$

where K_m represents the intrinsic dissociation constant of micelles with aggregation number m, and G_{el} means the electrostatic free energy of a micelle. k is the Boltzmann constant and T is the temperature.

Suppose that the apparent dissociation constant for a micellar solution, $(K_a)_{app}$, is represented by

$$(pK_a)_{app} = pH + \log\left(\frac{\alpha}{1 - \alpha}\right) \quad (5)$$

If the surfactant concentration is much higher than the critical micelle concentration, that is, $C \gg C_0$, then it follows that

$$\alpha \approx \alpha_m \quad \text{and} \quad (pK_a)_{app} \approx (pK_m)_{app} \quad (6)$$

If $(pK_a)_{app}$ is extrapolated to $\alpha = 0$, that is, if $(pK_m)_{app}$ is reduced

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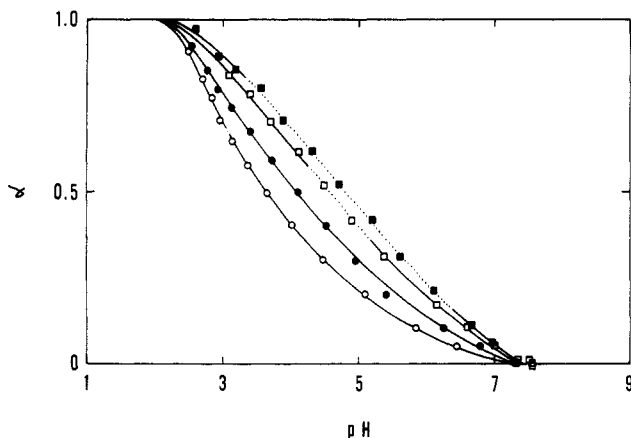
Figure 6. The titration curve for aqueous NaCl solutions of dimethyl-oleylamine oxide with the surfactant concentration of 0.30×10^{-2} g cm^{-3} at 25 °C. NaCl concentration: O, 0 M; ●, 0.01 M; □, 0.05 M; ■, 0.10 M.

to $\alpha_m = 0$, the value of pK_m can be obtained.

Figure 5 shows the pH dependence of the α values for 0.05 M NaCl solutions with different surfactant concentrations above 0.1 $\times 10^{-2}$ g cm^{-3}. There is no surfactant concentration dependence of the titration curve and, therefore, of the $(pK_a)_{app}$ value at given α values. The surfactant concentration is sufficiently higher than the critical micelle concentration at any pH, but the micelles are still sufficiently dilute to behave independently. Hence, eq 6 is applicable for these surfactant concentrations. The independence of the α–pH relation on the surfactant concentration is also observed for 0.10 M NaCl solutions with surfactant concentrations above 0.10×10^{-2} g cm^{-3}, which is again twenty times higher than the critical micelle concentration.

The titration curves for various NaCl solutions with surfactant concentration of 0.30×10^{-2} g cm^{-3} are shown in Figure 6. The curves depend on the NaCl concentration, and they shift to higher pH with an increase of NaCl concentration. This means that the micelles are more readily protonated in more concentrated NaCl solutions, when the pH is identical.

The titration curves of surfactant solutions are shown in Figure 7, where the values of $(pK_a)_{app}$ are plotted against α. The $(pK_a)_{app}$ values increase with a decrease of α and with an increase of NaCl concentration. The extrapolation to $\alpha = 0$ gives the pK_m value for each NaCl concentration.

The pK_m values were obtained as 5.44, 5.76, 5.91, and 5.94 for 0, 0.01, 0.05, and 0.10 M NaCl solutions, respectively. The pK_m values increase with increasing NaCl concentration, as observed for dimethyldodecylamine oxide.[18] While the pK_m value of dimethyloleylamine oxide micelles in water is lower than that of dimethyldodecylamine oxide micelles in water, the pK_m in aqueous NaCl solution is slightly higher for dimethyloleylamine oxide micelles.

The dotted portions in Figures 5–7 represent a region where liquid–liquid phase separation occurs. Liquid–liquid phase separation occurs at α from 0.35 to 0.55 for 0.05 M NaCl solutions and α from 0.15 to 0.83 for 0.10 M NaCl solutions. With reference to Figure 4, it is also obvious that a 0.05 M NaCl solution with 10^{-3} N HCl separates into two phases at pH 4–5, corresponding to α from 0.7 to 0.4. The phase separation occurs at wider pH and α regions in 0.10 M NaCl with 10^{-3} and 10^{-2} N HCl.

Discussion

The LCST and the Hydrophobicity of Surfactant. The existence of the lower consolute phase boundary can be observed in dilute aqueous solutions of some surfactants that can form hydrogen bonds with water, when it is at proper temperatures. It is likely that the appearance of a consolute boundary is strongly dependent on the balance of hydrophobicity and hydrophilicity

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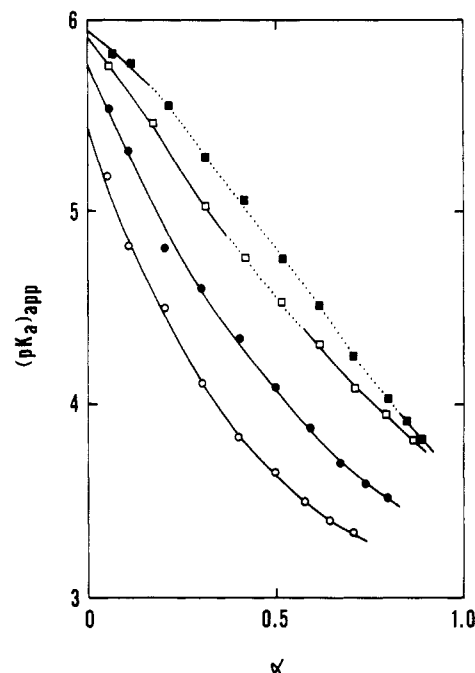
Figure 7. The values of $(pK_a)_{app}$ plotted against α for aqueous NaCl solutions of dimethyloleylamine oxide with the surfactant concentration of 0.30×10^{-2} g cm^{-3} at 25 °C. The symbols have the same meaning as those in Figure 6.

of the surfactant as well as on the salt species and its concentration.

It is known that poly(oxyethylene) alkyl ethers have a cloud point in water, above which temperature their aqueous solutions separate into two liquid phases.[10] The cloud point can be identified with the lower consolute temperature, and approximately with the LCST.

Several investigations on the phase behavior have been carried out with aqueous solutions of monodisperse oligooxyethylene alkyl ethers (abbreviated as C_nE_x).[4,6–9,11,12] With increasing length, n, of the alkyl chain, the LCST of the hexa(oxyethylene) alkyl ether decreases: 71 or 76 °C for C_8E_6, 59 °C for $C_{10}E_6$, and 48 °C for $C_{12}E_6$. With decreasing number, x, of oxyethylene groups, the LCST decreases systematically: 77 °C for $C_{12}E_8$, 48 °C for $C_{12}E_6$, 26.5 °C for $C_{12}E_5$, and 4 °C for $C_{12}E_4$. It is also likely that the surfactant concentration at the LCST is higher for longer oligooxyethylene chains, as well as for shorter alkyl chains.

A similar correlation of the LCST and its surfactant concentration with the length of alkyl chain is observed for aqueous solutions of dimethylalkylphosphine oxide.[5,9]

When a simple salt is added to aqueous solutions of nonionic surfactants, the cloud point is altered, depending on the salt species and concentration. For poly(oxyethylene) nonylphenyl and dodecyl ethers having an average number of oxyethylene groups, 15 and 6.3, respectively, Maclay,[10] Schick,[13] and Tokiwa and Matsumoto[14] observed such effects with various kinds of simple salts. The addition of NaCl generally lowers cloud points systematically.

It has been observed for oligooxyethylene alkyl ethers that, as the alkyl chain length is longer, rodlike micelles are readily formed at lower surfactant concentrations.[4,19] Accordingly, it would be natural to correlate the lower LCST and its location at a lower surfactant concentration with the formation of longer rodlike micelles. Although this correlation of the LCST with the presence of rodlike micelles has been strongly disputed for aqueous solutions of oligooxyethylene alkyl ether in view of the interpretation of light scattering[5,12,20] and small angle neutron scattering,[21,22] there exists also strong support for the formation of rodlike micelles.[23,24]

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We have measured the micelle molecular weight of dimethyloleylamine oxide in aqueous NaCl solutions at 25 °C and observed the formation of very long, flexible rodlike micelles and their growth with increasing NaCl concentration.[1-3] This observation can be most adequately correlated with the lowered consolute NaCl concentration and also with the lowered consolute temperature. As compared with the micelle size of other surfactants showing an LCST, the micelle molecular weight of dimethyloleylamine oxide is generally large, especially in the presence of NaCl. Then, we may attribute the lowering of the LCST, especially its location at lower surfactant concentrations with the consequent asymmetry of the consolute phase boundaries, to the presence of large rodlike micelles.

"Closed Loop" Consolute Phase Diagram. Aqueous 0.05 M NaCl solutions of dimethyloleylamine oxide in the presence of 10^{-3} N HCl have an LCST at a low temperature (−13 °C) and a UCST at a high temperature (68 °C). This gives a "closed loop" phase diagram for liquid–liquid phase separation, as shown in Figure 3.

This kind of a "closed loop" diagram has been observed for aqueous mixtures of simple compounds such as nicotine,[25] lutidines,[26] ethylpyridine,[26] and *n*- and isobutyl cellosolves.[27] For such behavior the following view is now accepted. Hydrogen bonding between the solute molecule and water molecule plays an important role in energetically stabilizing the solute in water at low temperatures, while restricting the orientational freedom,[28] but it is disrupted by the effect of disorientation entropy with rising temperature, making the mixture energetically unfavorable, and leading to liquid–liquid phase separation. At much higher temperatures, however, the mixture becomes entropically stable, overcoming the unfavorable energy, and again the solute forms a homogeneous mixture with water. This scheme has been quantitatively treated by the quasi-chemical method,[29,30] the decorated lattice method,[31-33] the Potts method,[34-36] and the Bethe method.[37] Thus the lower consolute phase boundary in aqueous solutions can be regarded as part of a "closed loop" phase boundary for liquid–liquid phase separation.

Even with water-soluble polymers such as poly(ethylene glycol) and poly(propylene glycol),[38,39] "closed loop" phase diagrams are obtained, if the degree of polymerization is low, while only lower phase boundaries are observed, if the degree of polymerization is high. In such cases the LCST (and UCST) are located at very low concentrations, reflecting the influence of the large difference in molecular size of the solute and water.

The same mechanism for phase separation would be operative, related to the hydrogen bonding between a polymeric solute and water. Hydrogen bonding of residues in such a polymer with water molecules plays a role in stabilizing the polymer in water at low temperatures. However, with rising temperature, hydrogen bonds are broken, the polymer in water is destabilized, and the aqueous solution of the polymer separates into two phases. Thus the occurrence of the LCST in aqueous solutions of poly(alkylene glycol) is caused by the specific interaction between the solute and water, i.e., by hydration or hydrogen bonding.

In aqueous solutions of nonionic surfactants such as oligooxyethylene alkyl ethers and dimethylalkylphosphine oxides, it

has been observed that large rodlike micelles are formed,[4,5,19] and these micelles can still form many hydrogen bonds with water molecules through the polar head group of each molecule in the micelle. A small amount of coexistent monomer would have only a small effect on the phase behavior. We may then anticipate that the same mechanism of phase separation as above holds for aqueous solutions of surfactant. In this case, however, we have to take adequate account of the effects of temperature on micelle size and shape.

The "closed loop" boundary curve does not always have a mirror image relation with respect to the LCST and UCST, and it is also often asymmetrical with respect to the solute concentration.[5,9,27,38,39] The "closed loop" profile for 0.05 M NaCl solutions of dimetyloleylamine oxide with 10^{-3} N HCl is asymmetric with both temperature and surfactant concentration and is qualitatively very similar to that for dimethylalkylphosphine oxide in water.[5,9] The lower consolute temperature for the aqueous NaCl solutions of dimethyloleylamine oxide at neutral pH is also very asymmetric with the surfactant concentration and is located at very low surfactant concentrations. The boundary curves expand with the addition of NaCl, because the micelle molecular weight becomes larger with an increase in NaCl concentration.[2,3]

The asymmetry of the phase diagram increases with increasing molecular weight of solute, accompanied by a rise of the UCST and a lowering of the LCST. Then the UCST and LCST also shift toward dilute solute compositions. It was observed for poly(ethylene glycol)[38] that the "closed loop" spreads to wider temperature and concentration regions with increasing degree of polymerization. A similar dependence of consolute boundary on alkyl chain length was shown to exist for dimethyldecyl- and dimethyldodecylphosphine oxide[5,9] which should be directly related to the size of the micelles. However, dimethyloctylphosphine oxide was not sufficiently hydrophobic to give any cloud point at all up to 200 °C. It was suggested for poly(ethylene glycol) in water[39] that the UCST and LCST become closer together with decreasing degree of polymerization and coalesce or disappear when the molecular weight is lower than 2140, giving complete miscibility over the whole concentration range.

We have shown by light scattering measurements at 25 °C[3] that the micelle molecular weight of dimethyloleylamine oxide is larger in 10^{-3} N HCl than in water, when NaCl of an equal concentration is present. Then we may expect that the lower consolute NaCl concentration could be lower at 10^{-3} N HCl. This is consistent with the phase diagrams shown in Figure 2. It is also relevant to note that the 10^{-3} N HCl solution of dimethyloleylamine oxide has a pH value around 5 and the amine oxide is half-neutralized in it. Dimethyldodecylamine oxide in aqueous solutions also gave the lowest consolute NaBr concentration, when it was nearly half-neutralized by HBr.[40]

Although we have not determined the micelle molecular weight of dimethyloleylamine oxide in 10^{-2} N HCl, because of the construction of our light scattering cell, it is quite likely that its micelle molecular weight is lower in 10^{-2} N HCl than in 10^{-3} N HCl. The reason is that there is much evidence that rodlike micelles in 10^{-3} N HCl are largely stabilized by hydrogen bonding between the amine oxides and the *N*-hydroxyammonium ions as well as by the hydrophobic interactions among them, while the electrostatic repulsion between the *N*-hydroxyammonium ions is dominant with rodlike micelles in 10^{-2} N HCl. This fact is also consistent with the phase diagrams observed in 10^{-3} and 10^{-2} N HCl, shown in Figure 2.

The Occurrence of Opalescence. The relation of consolute boundary to micelle size and shape has been discussed by many workers.[2-5,12,40] It was shown that the micelle size of hexa(oxyethylene)dodecyl ether in water and the dissymmetry of light scattering in its micellar solution increase as the LCST is approached.[4] The micelle molecular weight of dimethyldodecylphosphine oxide in water was rather less sensitive to the temperature; the molecular weight increased by 20% during the elevation of temperature from 1 to 30 °C.[5]

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Conversely, it was shown that the micelle molecular weight and axial ratio of rodlike micelles of dimethyldodecylamine oxide in 0.20 M NaBr at pH 3 appear to decrease with increasing temperature.[40] However, increases in molecular weight and length of rodlike micelles were observed as the pH approached the region of phase separation.

We have shown that the molecular weight and radius of gyration of micelles of dimethyloleylamine oxide in aqueous NaCl solutions are independent of the micelle concentration, when the solution is far more concentrated than the critical micelle concentration but yet not so concentrated as to produce opalescence or phase separation.[2,3]

The strong light scattering intensity and angular dissymmetry near the critical point can also be interpreted as critical opalescence.[40] Then light scattering intensity is contributed not only by the average square of the amplitude of the fluctuations but also by the average square of the gradient of the fluctuations.[41]

This additional long-range concentration fluctuation term becomes important near the critical point.

It was noted that the light scattering behavior of oligooxyethylene alkyl ether in water could be ascribed to critical concentration fluctuations;[12] the liquid–liquid phase transition for short alkyl chain homologues could be attributed to the interaction among small spherical micelles. For long alkyl chain homologues, there would be a large effect of micelle growth caused by the temperature rise, besides the effect of critical opalescence, since the concentration of anisotropic phase formation would not be very far from the concentration for liquid–liquid phase separation.

Visible opalescence phenomena were observed for aqueous NaCl solutions of dimethyloleylamine oxide at high surfactant concentrations, as shown in Figure 2. They are independent of liquid–liquid phase separation and could arise from the interaction between large micelles which might portend subsequent liquid crystal formation.

Registry No. $CH_3(CH_2)_7CH{=}CH(CH_2)_8N(CH_3)_2O$, 14351-50-9; NaCl, 7647-14-5; HCl, 7647-01-0.

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CHEMICAL KINETICS

## The Initial Process of the Oxidation of the Methyl Radical in Reflected Shock Waves

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The oxidation of the methyl radical was investigated in mixtures of C_2H_6–O_2–Ar and CH_3I–O_2–Ar behind reflected shock waves by monitoring the O atom, H atom, and OH radical in the temperature range from 1430 to 2150 K. Computer kinetic modeling of the experimental profiles yielded a rate constant for $CH_3 + O_2 \rightarrow CH_3O + O$ (2) of $k_2 = 10^{14.35} \exp(-33.7 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value was essentially the same as those reported previously. For the competing reaction $CH_3 + O_2 \rightarrow CH_2O + OH$ (3), experiments showed a low sensitivity to the assumed k_3 value and the following rate constant was evaluated with an uncertainty factor of 5: $k_3 = 10^{11.50} \exp(-9.0 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These results were discussed in terms of ab initio MO calculations by Kamiya et al.

Introduction

In the oxidation of hydrocarbons, the methyl radical plays an important role because of its stability compared to the larger radicals that decompose rapidly before they react with oxygen. The oxidation mechanism of the CH_3 radical involves $CH_3 + O$ and $CH_3 + O_2$. The former is well-known to produce $CH_2O + H$ with an established rate constant and follows a series of reaction for formaldehyde.[1] The latter involves two competing reactions:

$$CH_3 + O_2 \rightarrow CH_3O + O \qquad (2)$$
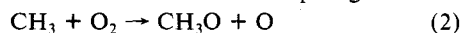
$$\Delta H_r^{\circ}{}_{298} = 28.2 \text{ kcal mol}^{-1}$$

$$CH_3 + O_2 \rightarrow CH_2O + OH \qquad (3)$$
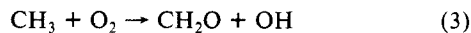
$$\Delta H_r^{\circ}{}_{298} = -53.2 \text{ kcal mol}^{-1}$$

Experimental data reported for k_2 have been in agreement with each other since the first determination by Brabbs and Brokaw,[2] giving reasonable values for the activation energy ranging from 26 to 31 kcal mol^{-1}. On the other hand, the experimental values for k_3, which has been used by many kineticists as the dominant

route, are widely scattered over a 20-fold range around 2000 K. Although the generally accepted k_3 value is larger than k_2 by about an order of magnitude, recent shock tube studies gave lower values for k_3 than k_2.[3,4] According to recent ab initio MO calculations on the transition states of these channels, an excited peroxide radical CH_3OO^* is produced, which then rearranges to give the products through separate pathways.[5]

In this paper, we investigate the $CH_3 + O_2$ reaction behind reflected shock waves and examine the two competing channels on the basis of recent MO calculations.

Experimental Section

Shock Tube System. A time-resolved O-atom, H-atom, and OH radical absorption study was performed in a 9.4-cm-i.d. pressurized driver shock tube. The tube had a 4.5-m long driven section made of stainless steel, which was pumped down by a liquid nitrogen trapped 6-in. diffusion pump to less than 1×10^{-6} torr.

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