

The pH Dependence of Upper and Lower Consolute Phase Boundaries for Aqueous NaCl Solutions of Dimethyloleylamine Oxide

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The liquid-liquid phase separation diagrams for dilute aqueous NaCl solutions of dimethyloleylamine oxide have been obtained at temperatures between 5 and 85°C for pH less than 8 at different NaCl concentrations. The liquid-liquid phase separation is induced between pH 3.85 and 4.9 at temperatures less than 30°C, when the NaCl concentration is 0.05 *M* and the surfactant concentration is 0.30×10^{-2} g cm⁻³, and it occurs over wider regions of pH and temperature with increasing NaCl concentration. The critical value of lower consolute NaCl concentration, below which a homogeneous solution is formed, is 0.048 *M* for pH 4.6 at 25°C.

The consolute phase boundary is also given as a function of surfactant concentration. On the temperature-surfactant concentration phase diagrams, an upper critical solution temperature (UCST) is observed for both 0.05 and 0.10 *M* NaCl solutions, and it decreases with decreasing pH. Similarly, a lower critical solution temperature (LCST) observed for 0.10 *M* NaCl solutions decreases with a decrease in pH. Since the LCST would be lower than the UCST at a given pH, the phase separation profile should be a "closed loop." The pH dependence of liquid-liquid phase separation is discussed in relation to the hydration of rodlike micelles and the hydrogen bonding between amine oxide molecules and *N*-hydroxyammonium ions in a micelle. © 1986 Academic Press, Inc.

INTRODUCTION

Aqueous solutions of nonionic surfactants such as oligooxyethylene alkyl ether (1-7) and dimethyldodecylphosphine oxide (8) undergo liquid-liquid phase separation at a lower critical solution temperature (LCST). The LCST may be related to the specific interaction such as hydrogen bonding between solute and solvent (1, 9-11); that is, surfactant-water attractive interaction causing specific molecular orientation produces a homogeneous solution at lower temperatures.

The phase diagram for aqueous solutions of oligooxyethylene alkyl ether exhibits the LCST which ranges from the freezing point of water to its boiling point, depending on the alkyl and oxyethylene chain lengths. The long alkyl chain favors the repulsive interaction between micelle and water, and the short oxy-

ethylene chain suppresses the formation of hydrogen bonding between surfactant and water, both influencing favorably the phase separation at the LCST.

For aqueous solutions of dimethyldecyl- and dimethyldodecylphosphine oxide, which are nonionic at neutral pH and can form hydrogen bonds with water at its polar head group, liquid-liquid phase separation strongly depends on the alkyl chain length: the LCST of the aqueous solution of dimethyldecylphosphine oxide was higher than that of dimethyldodecylphosphine oxide, and no phase separation for the aqueous solution of dimethyloctylphosphine oxide was observed even at temperatures up to 200°C (5, 8).

The phase-separated solutions of dimethyldecyl- and dimethyldodecylphosphine oxide (5, 8) and tetraoxyethylene and pentaoxyethylene decyl ether (5) are again miscible at higher temperatures around 170-300°C, and this phenomenon can be attributed to the stronger

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effect of entropy of mixing as in the usual binary mixtures. The upper critical solution temperature (UCST) is higher than the LCST, and the temperature-concentration phase diagram exhibits a "closed loop" profile. The mechanism of occurrence of "closed loops" for surfactant solutions was discussed (5) in terms of the decorated lattice model (12-14).

Liquid-liquid phase separation was recently reported for aqueous solutions of some zwitterionic surfactants (15), for each of which the UCST was recorded at approximately room temperature.

The effect of pH on the phase separation profile was examined for 0.2 *M* NaBr solutions of dimethyldodecylamine oxide (16). The separation into two isotropic phases occurred in the pH range 4.4-5.4 at room temperature, and a homogeneous solution was observed above 32°C.

We have recently investigated phase separation of dilute aqueous NaCl solutions of dimethyloleamine oxide, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8\text{N}(\text{CH}_3)_2\text{O}$, in the absence of added HCl and in the presence of 10^{-3} and 10^{-2} *N* HCl, and found that a "closed loop" consolute phase boundary is formed in the presence of 10^{-3} *N* HCl and 0.05 *M* NaCl (17).

In order to see the details of phase separation behavior, we examine the dilute aqueous NaCl solutions of dimethyloleamine oxide at a different pH in the present work. The phase diagram at constant surfactant concentration is obtained for temperature versus pH at different NaCl concentrations. We propose a molecular mechanism for the phase separation based on the hydrogen bonding in micelles of dimethyloleamine oxide.

EXPERIMENTAL

The sample of dimethyloleamine oxide was the same as previously used (17-21). The purity of the surfactant was examined by the surface tension: there was no minimum at the critical micelle concentration on a surface tension curve (21). Special grade NaCl was ignited for 1 h. Water was redistilled from alkaline KMnO_4 .

Aqueous NaCl solutions of dimethyloleamine oxide were prepared, and an HCl solution was added to obtain solutions with the desired pH. The concentration of surfactant was varied from 0.01×10^{-2} to 0.60×10^{-2} g cm^{-3} , and that of NaCl was changed up to 1.0 *M*. Each solution was kept overnight at room temperature ($25 \pm 1^\circ\text{C}$), and their pH was measured on an Iwaki Glass pH/ion meter M-225 under a nitrogen atmosphere. The pH value observed at room temperature was used at different temperatures under the assumption that it was not greatly affected by temperature.

Solutions were incubated in a water bath at a given temperature for 4 h, within which phase equilibrium had been attained. Temperature was varied from 5 to 85°C. The appearance of phase separation was verified by visual inspection.

RESULTS

First, the concentration of dimethyloleamine oxide in aqueous NaCl solutions was kept at 0.30×10^{-2} g cm^{-3} , and the temperatures of liquid-liquid phase separation were measured against pH at different NaCl concentrations, as shown in Fig. 1a. Phase separation in the presence of 0.05 *M* NaCl is observable at pH 3.85-4.9 when the temperature is low, and the solutions are homogeneous above 30°C. The pH region for phase separation becomes wider as the NaCl concentration increases, and it shifts to a higher pH region with rising temperature. Two separated phases are not miscible even at 85°C for 0.10-1.0 *M* NaCl solutions.

The logarithm of molar concentration of NaCl for liquid-liquid phase separation against pH is drawn in Fig. 1b, which is obtained on the basis of Fig. 1a. The lower consolute NaCl concentration has a minimum at pH 4.25-5.5, and it depends on the temperature between 5 and 65°C: the minimum rises from 0.045 to 0.06 *M* with an increase in temperature and is 0.048 *M* at 25°C. At higher temperatures the two-phase region shifts to a higher pH region.

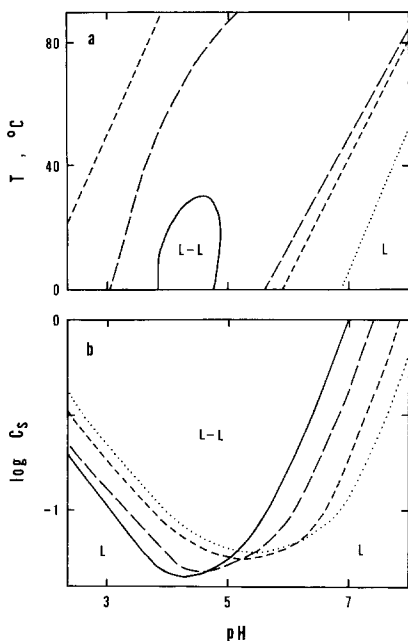


FIG. 1. Liquid-liquid phase separation for aqueous NaCl solutions of dimethyloleylamine oxide with a surfactant concentration of $0.30 \times 10^{-2} \text{ g cm}^{-3}$. L, Homogeneous region; L-L, two-phase region. (a) Temperature-pH relation. NaCl concentration (M): —, 0.05; --, 0.10; ---, 0.20; ···, 1.0. (b) Logarithm of NaCl molar concentration-pH relation. Temperature ($^{\circ}\text{C}$): —, 5; --, 25; ---, 45; ···, 65.

If the dependence of consolute temperature on the NaCl concentration is examined at constant pH on the basis of Fig. 1a, the upper consolute boundary is observed only at low pH and lowers with diluting NaCl concentration, while the lower consolute boundary is observable only at high pH and rises with increasing NaCl concentration.

Next, the effect of surfactant concentration on the liquid-liquid phase separation was examined for 0.05 and 0.10 M NaCl solutions. The variation of the phase separation profile associated with temperature and pH is manifest but is rather small at surfactant concentrations of $(0.01\text{--}0.60) \times 10^{-2} \text{ g cm}^{-3}$. The results are replotted in terms of the pH for phase separation against the surfactant concentration at constant temperature, as shown in Fig. 2.

As seen in Fig. 2, the 0.05 M NaCl solution at 15°C separates into two isotropic phases between pH 3.75 and 5.0. The phase boundary at 15°C depends slightly on the surfactant concentration. The two-phase region becomes narrower at 25°C and disappears at surfactant concentrations above $0.26 \times 10^{-2} \text{ g cm}^{-3}$ at 35°C . Liquid-liquid phase separation for 0.10 M NaCl solution occurs between pH 3 and 6 at 5°C . The region of phase separation shifts to a higher pH with a rise in temperature. The phase boundary at $5\text{--}45^{\circ}\text{C}$ depends slightly on the surfactant concentration.

The temperature for the phase separation is illustrated as a function of surfactant concentration at constant pH. Figures 3 and 4 show the phase diagrams in the presence of 0.05 and 0.10 M NaCl, respectively. For 0.05 M NaCl solutions at pH 4.0, the UCST is 30°C , having the surfactant concentration of $0.03 \times 10^{-2} \text{ g cm}^{-3}$. The UCST rises with an increase in pH and is 46°C for pH 4.75. The 0.10 M NaCl solution at pH 3.5 has the UCST at 52°C , which would be higher than that for the 0.05 M NaCl solution at the corresponding pH. At high pH, the lower consolute boundary is developed for 0.10 M NaCl solutions, and the LCST rises with an increase in pH.

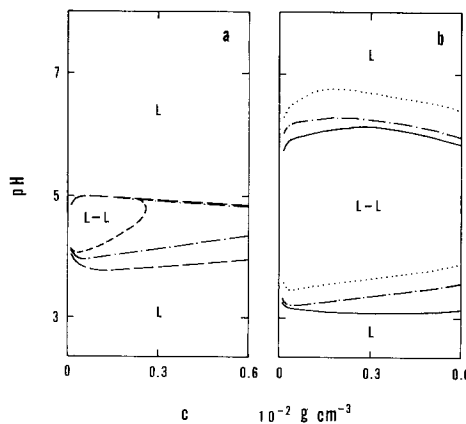


FIG. 2. Liquid-liquid phase separation for aqueous NaCl solutions of dimethyloleylamine oxide: pH-surfactant concentration relation. L, Homogeneous region; L-L, two-phase region. NaCl concentration (M): (a) 0.05; (b) 0.10. Temperature ($^{\circ}\text{C}$): —, 5; --, 15; —·—, 25; ···, 35; ····, 45.

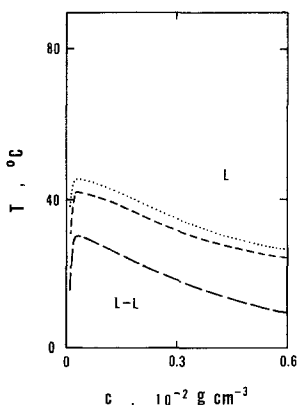


FIG. 3. Liquid-liquid phase separation for 0.05 *M* NaCl solutions of dimethyloleylamine oxide: temperature-surfactant concentration relation. L, Homogeneous region; L-L, two-phase region. —, pH 4.0 (α_m 0.63); ---, pH 4.5 (α_m 0.52); ···, pH 4.75 (α_m 0.45).

DISCUSSION

The Occurrence of Liquid-Liquid Phase Separation

We have reported that an aqueous NaCl solution of dimethyloleylamine oxide at neutral pH separates into two liquid phases and the LCST decreases from 19 to 3°C with increasing the NaCl concentration from 1.0 to 4.0 *M* (17). A similar effect of the addition of NaCl was reported for the LCST of an aqueous solution of polyoxyethylene alkyl ether (22, 23).

The consolute phase boundaries of aqueous NaCl solutions of dimethyloleylamine oxide are induced at lower NaCl concentrations, as the pH decreases and some surfactant molecules are protonated to form dimethyloleyl *N*-hydroxyammonium ions. The 0.05 *M* NaCl solution of dimethyloleylamine oxide induces the liquid-liquid phase separation around pH 4–5 at temperatures below 30°C, as seen in Fig. 1a.

A phase diagram similar to that for 0.05 *M* NaCl solutions of dimethyloleylamine oxide (Fig. 1a) was obtained for 0.2 *M* NaBr solutions of dimethyldodecylamine oxide (16). Separation of the latter solutions into two isotropic phases occurred at pH 4.4–5.4 at room temperature, and its upper critical temperature

was 32°C at pH 4.9. NaCl is less effective for the phase separation behavior than NaBr, and the presence of 0.2 *M* NaCl did not cause phase separation at 27°C for dimethyldodecylamine oxide (16). Then dimethyloleylamine oxide would have a greater tendency for the phase separation than dimethyldodecylamine oxide, because the repulsive interaction between the micelle and water is stronger for dimethyloleylamine oxide.

The liquid-liquid phase separation in aqueous NaCl solutions of dimethyloleylamine oxide is induced over a wider range of pH with increasing NaCl concentration, similar to that of aqueous NaBr solutions of dimethyldodecylamine oxide (16). The critical value of the lower consolute NaCl concentration is observed around pH 4.6 at 25°C for aqueous NaCl solutions of dimethyloleylamine oxide. This pH value is close to 4.9 for dimethyldodecylamine oxide in an aqueous NaBr solution at 27°C, although the critical salt concentration is lower for the former surfactant owing to its hydrophobicity.

Shape of the Consolute Phase Boundary

The temperature-surfactant concentration phase diagram for 0.05 *M* NaCl solutions of dimethyloleylamine oxide, shown in Fig. 3, suggests the occurrence of the UCST below

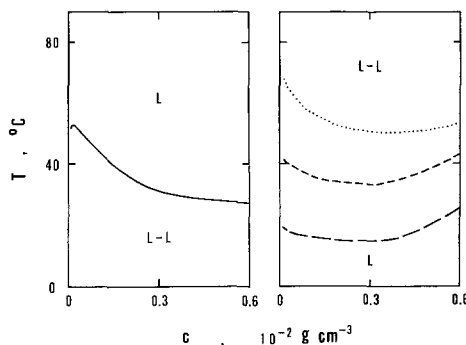


FIG. 4. The liquid-liquid phase separation for 0.10 *M* NaCl solutions of dimethyloleylamine oxide: temperature-surfactant concentration relation. L, Homogeneous region; L-L, two-phase region. —, pH 3.5 (α_m 0.80); ---, pH 6.5 (α_m 0.14); ···, pH 7.0 (α_m 0.06).

pH 5 in an attainable temperature region. The UCST decreases as the pH is decreased.

For 0.10 *M* NaCl solutions, the UCST is observed at lower pH and the LCST at higher pH, as shown in Fig. 4. The LCST decreases with a decrease in pH, and the LCST at pH 3.5 would be lower than the UCST at the same pH, as can be concluded from Fig. 4, although the LCST at pH 3.5 cannot be attained. Hence, the temperature-surfactant concentration profile of phase separation at constant pH would be a "closed loop."

The "closed loop" shifts to a lower temperature with a decrease in pH, since the UCST for a 0.05 *M* NaCl solution and the LCST for a 0.10 *M* NaCl solution decrease with decreasing pH. The "closed loop" broadens with an increase in NaCl concentration, because the UCST for a 0.10 *M* NaCl solution would be higher than that for a 0.05 *M* NaCl solution if compared at the same pH.

The effect of salt on the "closed loop" is consistent with the observation which was previously found for aqueous NaCl solutions of dimethyloleylamine oxide at constant HCl concentration (17). The 0.05 *M* NaCl solutions with 10^{-3} *N* HCl provided a "closed loop" profile with the LCST at -13°C and the UCST at 68°C , and the "closed loop" broadened for the 0.10 *M* NaCl solutions with 10^{-3} *N* HCl.

If aqueous solutions of surfactants exhibit the LCST between the freezing and boiling points of water, the UCST should be located at a high temperature, and the UCST cannot be realized unless the solution is heated in a sealed vessel, i.e., under an elevated pressure. On the other hand, the LCST cannot be observed if it is at a temperature lower than the freezing point. In the case of dimethyloleylamine oxide both cases were encountered, depending on pH, and thus it was difficult to observe the whole "closed loop."

Effect of Hydrogen Bonding and Composition of Micelles

In our previous work on light scattering (18–20) we have observed that dimethyloleylamine

oxide forms rodlike micelles in aqueous solutions, even without added salt. The micelle molecular weight strongly depends on the concentrations of NaCl and HCl, and is slightly dependent on the surfactant concentration far higher than the critical micelle concentration, where monomeric surfactants are negligible and micellar surfactants mainly contribute to the solution properties. Micelle size becomes independent of surfactant concentration in 0.05 and 0.10 *M* NaCl when the surfactant concentration is higher than 0.1×10^{-2} g cm^{-3} ; micelles are largest in 10^{-3} *N* HCl, where they are half-protonated.

Titration curves of aqueous NaCl solutions of dimethyloleylamine oxide are independent of the surfactant concentration at a given NaCl concentration, as long as the surfactant concentration is much higher than the critical micelle concentration (17). The surfactant concentration above which the titration curve becomes nearly independent of the surfactant concentration is reported as only 3.3 times higher than the critical micelle concentration for an aqueous NaCl solution of dimethyldodecylamine oxide (24). Then the degree of protonation of dimethyloleylamine oxide in aqueous NaCl solution should be constant for a given pH, if the surfactant concentration is higher than 0.01×10^{-2} g cm^{-3} . Thus the degree of protonation of a micelle, α_m , at a given NaCl concentration should be definite at the pH in the surfactant concentration region examined for phase separation, as given in Figs. 3 and 4.

The observed behavior of phase separation should be related to the behavior of mixed micelles consisting of amine oxide molecules and *N*-hydroxyammonium ions. Then hydrogen bonding between polar head groups of dimethyloleylamine oxide molecules in a micelle and water molecules must play an important role in liquid-liquid phase separation.

At neutral pH where the degree of protonation of the micelle is zero, nonionic micelles are present in aqueous solutions, strongly interacting with water through hydrogen bonds at low temperature, as shown in Fig. 5a. The

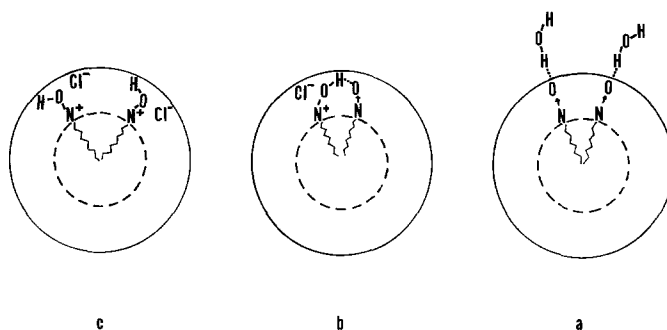


FIG. 5. Schematic representation of hydrogen bonds formed on rodlike micelles (cross section) of dimethyloleylamine oxide with different degrees of protonation. (a) Neutral pH, $\alpha_m \sim 0$; (b) pH 4–5, $\alpha_m \sim 0.5$; (c) acid pH, $\alpha_m \sim 1.0$.

nonionic micelles undergo dehydration with rising temperature, so that the solution finally separates into two phases at high temperature, if the micelle size is sufficiently large in the presence of NaCl.

With decreasing pH the protonation of micelles occurs and mixed micelles are formed. The micelle size becomes larger, and the lower consolute boundary is lowered.

Half-protonation of amine oxide yields equal amounts of amine oxide molecules and *N*-hydroxyammonium ions. We can then imagine surfactants to be in the most favorable situation for intermolecular hydrogen bonding, as illustrated in Fig. 5b. The amine oxide group and the *N*-hydroxyammonium ion are linked by a hydrogen bond which promotes the intermolecular association and leads to the formation of the largest rodlike micelle. The molecular consideration supports possible formation of a hydrogen bond between the O atom of the amine oxide molecule and the O–H group of the *N*-hydroxyammonium ion.

As the degree of protonation increases more than one-half, an excess of *N*-hydroxyammonium ions is present in a micelle, as shown in Fig. 5c, and cationic micelles interact only weakly with water, partly owing to the counterion binding on a micelle. The micelle size becomes smaller by the increased electrostatic repulsion between ionic surfactants in a micelle. The ionic micelles, which are less hydrated, can entropically dissolve in water at

high temperatures, and the phase separation is induced at low temperatures by the attractive interaction energy between micelles which are electrically shielded by the counterion binding, in addition to the repulsive interaction between micelle and water.

The presence of NaCl in a micellar solution partially destroys the hydration and reduces the electrostatic repulsion between micelles. Thus it promotes the growth of micelle size and the phase separation of solution, although its effects should differ from each other depending on whether the degree of protonation is higher or lower than one-half.

The liquid–liquid phase separation for aqueous solutions of zwitterionic surfactants such as alkylammoniopropyl sulfates exhibited the UCST at temperatures amenable to experiments (15). The UCST increases with increasing alkyl chain length, and the upper consolute boundary is rather symmetric against surfactant concentration. The phase separation cannot be explained by the dehydration, since it was reported that hydration remains relatively high even at high temperatures. It can be attributed to the prevalence of mixing entropy over intermicellar attraction, which is adequately caused by the intramolecular shielding of micelle charges, as in the case of micellar solutions of dimethyloleyl *N*-hydroxyammonium chloride. However, the rather symmetric shape of the phase boundary is caused by the fact that the micelles are small

and spherical, unlike in the case of micellar solutions of dimethyloleyl *N*-hydroxyammonium chloride.

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