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Liquid-Liquid Phase Separation in Dilute Aqueous Solutions of Surfactants: The Effect of Added Salt

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The salt-induced liquid-liquid phase separation in dilute aqueous solutions of dodecyl-, tetradecyl-, and hexadecyldimethylammonium chlorides or bromides ($C_{12}DAC$, $C_{14}DAC$, $C_{16}DAC$, $C_{12}DAB$, $C_{14}DAB$) and dodecylammonium chloride ($C_{12}AC$) has been observed and compared with that of hepta(oxyethylene) dodecyl, tetradecyl, and hexadecyl ethers ($C_{12}E_7$, $C_{14}E_7$, $C_{16}E_7$). While $C_{12}DAC$, $C_{14}DAC$, and $C_{14}DAB$ present the lower consolute phase boundary, similar to nonionic surfactants, $C_{16}DAC$ and $C_{12}DAB$ give a closed loop boundary and $C_{12}AC$ shows the upper consolute phase boundary. The effect of added salt on phase separation is examined and discussed on the basis of salting-out power and lyotropic series.

Introduction

The liquid-liquid phase separation of aqueous surfactant solutions has been reported mainly for nonionic surfactants.[1-9] Aqueous solutions of oligo(oxyethylene) alkyl ethers separate into two homogeneous solutions above a certain lower critical solution temperature (LCST), which appears usually between the freezing point and the boiling point, depending on alkyl and oxyethylene chain lengths. On the other hand, aqueous solutions of tetra(oxyethylene) and penta(oxyethylene) decyl ethers are again miscible at much higher temperatures than the boiling point.[5] Since the upper critical solution temperature (UCST) is higher than the LCST, the temperature-surfactant concentration phase diagram exhibits a closed loop profile.

Dimethyldecyl- and dimethyldodecylphosphine oxides are nonionic at neutral pH, and their aqueous solutions present the liquid-liquid phase separation profile of a closed loop type, strongly depending on alkyl chain length.[5,10]

We have examined the phase separation in dilute aqueous NaCl solutions of dimethyloleylamine oxide and observed the consolute phase boundary of a closed loop type for solutions with 10^{-3} N HCl and 0.05 M NaCl.[11] The UCST and the LCST both decrease with lowering pH.[12] The effect of pH on liquid-liquid phase separation has been reported for 0.2 M NaBr solutions of dimethyldodecylamine oxide.[13]

The liquid-liquid phase separation of aqueous solutions of dimethylalkylamine oxide was induced on the presence of salt and enhanced with increasing salt concentration.[11-13] The effect of various additives such as simple salts, surfactants, and organic liquids on the consolute phase boundary has been reported by several workers.[14-19]

The consolute phase boundary also has been reported for aqueous solutions of some zwitterionic surfactants,[20] which presents the UCST around room temperature.

In this work, we report the salt-induced liquid-liquid phase separation for aqueous solutions of cationic surfactants, alkyldimethylammonium halides and alkylammonium halides and examine the effect of ionic properties in comparison with the nonionic surfactants, oligo(oxyethylene) alkyl ethers.

Experimental Section

The sample of $C_{12}DAB$ is the same as previously used.[21] $C_{12}DAC$ and $C_{12}AC$ were kindly gifted by Mr. H. Okuda of Nagoya Municipal Industrial Research Institute, Nagoya. $C_{14}DAC$, $C_{14}DAB$, and $C_{16}DAC$, which were kindly donated by Drs. K. Hattori and U. Nishimoto of Kao Corp., Inc., Tokyo and Wakayama, were recrystallized 3 times from an ethanol-acetone mixture and dried for 8 h in vacuo at 80 °C. Monodisperse $C_{12}E_7$, $C_{14}E_7$, and $C_{16}E_7$ were purchased from Nikko Chemicals Co., Ltd., Tokyo. The purity of all surfactants was examined on gas chromatography.

NaCl and NaBr were ignited before use, and water was redistilled from alkaline potassium permanganate. Commercial sodium salicylate and sodium toluenesulfonate were used without any purification.

Preparation of solutions and construction of phase diagrams followed the procedure previously described in detail.[11,12] Temperature was changed between 0 and 99 °C and surfactant concentration ranged up to 10 wt %. The concentration by weight percent indicates gram/gram solution percent. The liquid-liquid phase separation boundary, the opalescence boundary, and the Krafft boundary were observed by visual inspection after solutions were kept at a desired constant temperature for 3 h or more.

Results

Liquid-Liquid Phase Separation. Figure 1 shows phase diagrams of temperature vs surfactant concentration of $C_{12}DAC$ for aqueous NaCl solutions with different NaCl concentrations. While solutions with NaCl concentrations up to 4 M are homogeneous over the whole temperature region, the liquid-liquid phase separation with the lower

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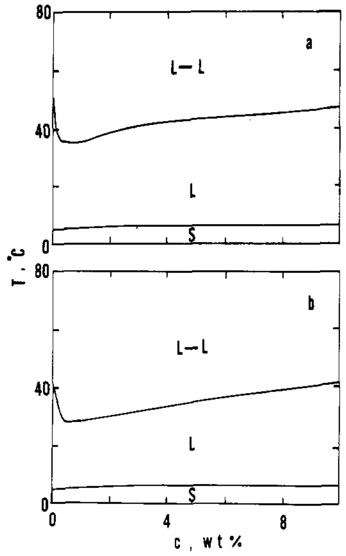

Figure 1. Phase diagrams for aqueous NaCl solutions of C_{12}DAC. NaCl concentration (M): a, 4.6; b, 4.8. L, homogeneous region; L–L, two-phase region; S, solid region.

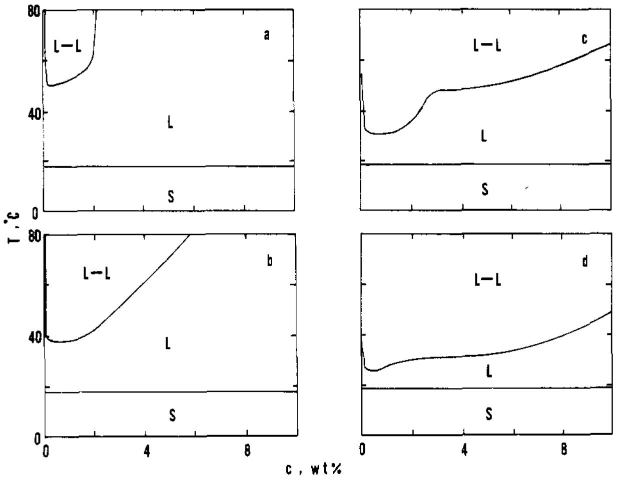

Figure 2. Phase diagrams for aqueous NaCl solutions of C_{14}DAC. NaCl concentration (M): a, 2.5; b, 2.6; c, 2.8; d, 3.0. Letters have same meanings as those in Figure 1.

consolute temperature appears for solutions of higher NaCl concentrations. The LCST is 36 °C in 4.6 M NaCl, and it lowers down to 28 °C in 4.8 M NaCl. The lower consolute boundary is asymmetric with respect to surfactant concentration: it rises abruptly with a decrease in surfactant concentration below 0.6–0.7 wt % but rises gradually with an increase in surfactant concentration above it.

The phase diagrams for aqueous NaCl solutions of C_{14}DAC are illustrated in Figure 2. The miscibility boundary with an LCST occurs at NaCl concentrations higher than 2.4 M. While the region of two-liquid-phases ranges only between surfactant concentrations at 0.1–2.1 wt % in 2.5 M NaCl, it spreads to lower temperatures and to higher surfactant concentrations with increasing NaCl concentration.

Figure 3 gives phase diagrams for aqueous NaCl solutions of C_{16}DAC. The liquid–liquid phase separation which develops for NaCl concentrations higher than 1.3 M displays a different profile from that of C_{12}DAC or C_{14}DAC: C_{16}DAC in 1.4 M NaCl exhibits an LCST at 35 °C and simultaneously a UCST at 92 °C. Therefore, the profile of consolute boundary is a closed loop, which is symmetric against temperature but is asymmetric against surfactant concentration. The closed loop spreads to a wider region of temperature and surfactant concentration with increasing NaCl concentration. In 1.5 M NaCl, the LCST is lower than the Krafft boundary and the UCST is higher than the boiling point. Then the LCST and the UCST have to be estimated by the extrapolation.

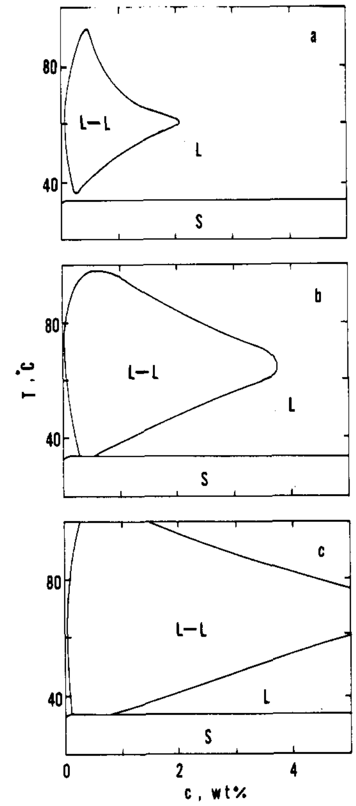

Figure 3. Phase diagrams for aqueous NaCl solutions of C_{16}DAC. NaCl concentration (M): a, 1.4; b, 1.45; c, 1.5. Letters have same meanings as those in Figure 1.

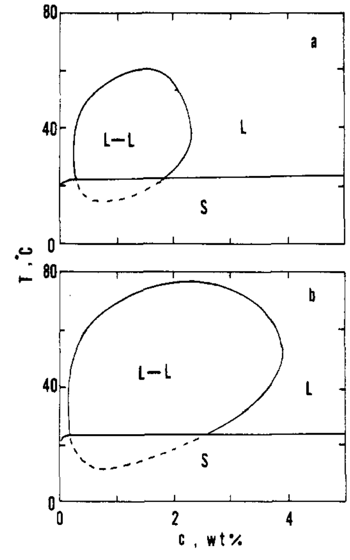

Figure 4. Phase diagrams for aqueous NaBr solutions of C_{12}DAB. NaBr concentration (M): a, 2.2; b, 2.3. Letters have same meanings as those in Figure 1. The phase boundary measured for supersaturated solutions is drawn by the dotted line.

The liquid–liquid phase separation with a closed loop profile also takes place in aqueous NaBr solutions of C_{12}DAB, as seen in Figure 4, although its shape is rather round, different from that of C_{16}DAC. It manifests at NaBr concentrations of 2.2 M or higher. The loop is wider

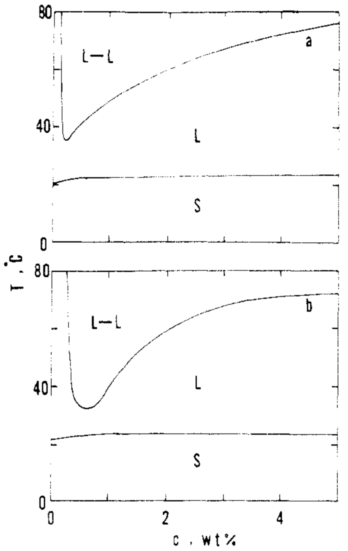

Figure 5. Phase diagrams for aqueous NaBr solutions of C$_{14}$DAB. NaBr concentration (M): a, 4.3; b, 4.4. Letters have same meanings as those in Figure 1.

for 2.3 M NaBr than for 2.2 M.

Figure 5 provides the phase diagrams for aqueous NaBr solutions of C$_{14}$DAB. Similar to that for C$_{12}$DAC or C$_{14}$DAC, the lower consolute boundary is observed with an asymmetric profile with respect to surfactant concentration. The LCST is 35 and 32 °C for 4.3 and 4.4 M NaBr, respectively. It should be noticed that the salt concentration added to aqueous C$_{14}$DAB solution for the induction of phase separation is very high as compared with that for C$_{14}$DAC, and it is almost equal to that for C$_{12}$DAC.

For C$_{12}$AC in aqueous NaCl solutions, a homogeneous solution is observed at temperature above the Krafft boundary in the vicinity of 20 °C for NaCl concentrations below 0.3 M. At 0.33 M NaCl, the region of liquid–liquid phase separation with the UCST exists above the Krafft boundary, as illustrated in Figure 6. The UCST rises with an increase in NaCl concentration.

Figure 7 shows the phase diagrams of CnE$_7$ in 1 M NaCl. They display the consolute phase boundary with an LCST at 43–53 °C, slightly decreasing with an increase in alkyl chain length. The lower consolute boundary rises scarcely with increasing surfactant concentration up to 10 wt %. The opalescence appears at temperature by 2 °C below the lower consolute boundary. The temperature region of lower consolute and opalescence boundaries decreases gradually with an increase in NaCl concentration. On the other hand, the addition of sodium salicylate and sodium toluenesulfonate raises the lower consolute boundary, in opposition to the addition of NaCl: the LCST for aqueous solutions of C$_{14}$E$_7$ is 89 °C in 0.3 M sodium salicylate and 94 °C in 0.5 M sodium toluenesulfonate.

The values of the LCST, the UCST, and the surfactant concentrations there, c_c, for aqueous solutions of surfactants examined are summarized in Table I.

Krafft Boundary. As seen in Figures 1–7, precipitation occurs with lowering temperature, except for C$_{12}$E$_7$ in 0–4 M NaCl and C$_{14}$E$_7$ in water. The Krafft boundary of alkyldimethylammonium halides is independent of surfactant concentration and salt concentration, although that of C$_{12}$AC and C$_n$$E_7$ rises slightly with an increase in salt concentration. As the alkyl chain length increases, the Krafft boundary rises, reflecting an increase in hydrophobicity. The values of the upper limit of Krafft boundary are included in Table I.

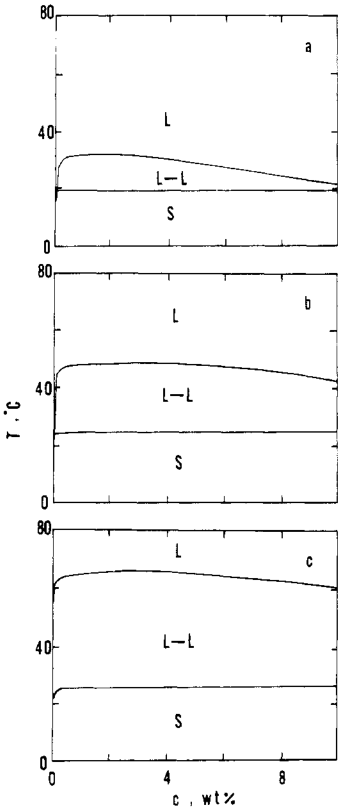

Figure 6. Phase diagrams for aqueous NaCl solutions of C$_{12}$AC. NaCl concentration (M): a, 0.33; b, 0.5; c, 0.7. Letters have same meanings as those in Figure 1.

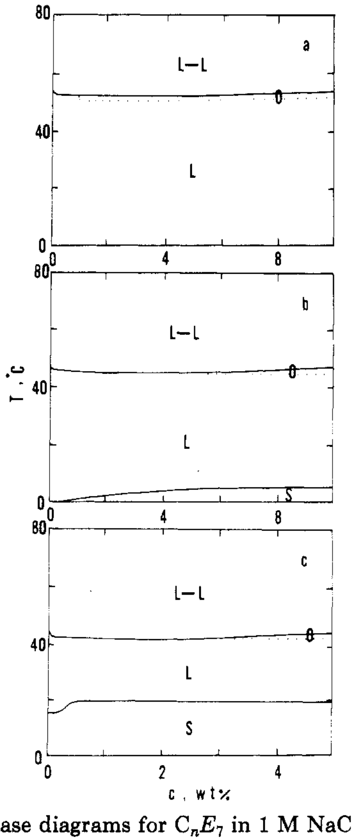

Figure 7. Phase diagrams for C$_n$$E_7$ in 1 M NaCl: a, C$_{12}$E$_7$; b, C$_{14}$E$_7$; c, C$_{16}$E$_7$. O, opalescent region. The other letters have same meanings as those in Figure 1.

Discussion

Above the critical micelle concentration, molecules of surfactant associate into micelles. The critical micelle concentration is (0.3–0.4) × 10^{-2} g cm^{-3} for C$_{12}$DAC, C$_{12}$-

Table I. LCST, UCST, and Upper Limit of Krafft Boundary for Aqueous Surfactant Solutions

surfactant	salt	C_s, M	LCST, °C	c_c, wt %	UCST, °C	c_c, wt %	upper limit of Krafft boundary, °C
$C_{12}DAC$	NaCl	4.6	36	0.6			6
		4.8	28	0.7			6
$C_{14}DAC$	NaCl	2.5	50	0.4			17.5
		2.6	37	0.5			17.5
		2.8	30	0.5			18
		3.0	26	0.4			18
$C_{16}DAC$	NaCl	1.4	35	0.3	92	0.45	33
		1.45	30^a	0.3^a	97	0.6	33
		1.5	25^a	0.3^a	105^a	0.6^a	33
$C_{12}DAB$	NaBr	2.2	15^b	0.7^b	61	1.5	23
		2.3	11^b	0.8^b	76	2.2	23
$C_{14}DAB$	NaBr	4.3	35	0.2			23
		4.4	32	0.6			23
$C_{12}AC$	NaCl	0.33			32	1.5	19
		0.5			48	2.0	25
		0.7			65	3.0	26
$C_{12}E_7$	NaCl	0	64	0.4–6			<0
		1	53	0.4–5			<0
		2	41.5	0.5–5			<0
		3	33	0.5–5			<0
		4	26	0.5–5			<0
$C_{14}E_7$	NaCl	0	57	0.5–2			<0
		1	45	2–4			6
		2	36	1–3			6.5
		3	28.5	0.3–4			22
$C_{16}E_7$	NaCl	0	53.5	0.5–1.5			14
		1	43	0.2–1			20
		2	34.5	0.1–1.5			22

[a] Extrapolated values. See the text. [b] Measured for supersaturated solutions.

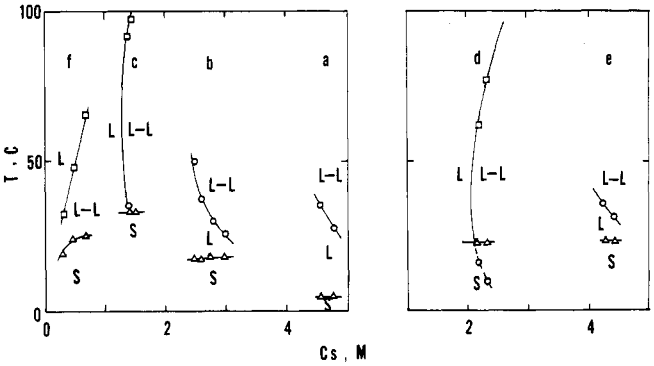

Figure 8. LCST, UCST, and the upper limit of the Krafft boundary for aqueous surfactant solutions as a function of salt concentration: ○, LCST; □, UCST; △, upper limit of Krafft boundary. a, $C_{12}DAC$; b, $C_{14}DAC$; c, $C_{16}DAC$; d, $C_{12}DAB$; e, $C_{14}DAB$; f, $C_{12}AC$. Letters have same meanings as those in Figure 1.

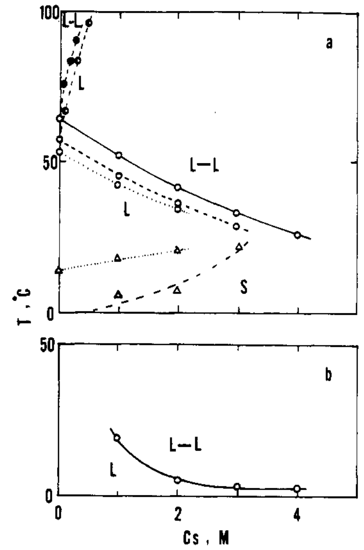

Figure 9. LCST and upper limit of Krafft boundary for aqueous surfactant solutions as a function of NaCl concentration: ○, LCST; △, upper limit of Krafft boundary. (a) —, $C_{12}E_7$; ---, $C_{14}E_7$; ···, $C_{16}E_7$; ◐, LCST for $C_{14}E_7$ in sodium toluenesulfonate; ●, LCST for $C_{14}E_7$ in sodium salicylate. (b) dimethyloleylamine oxide (ref 11). Letters have same meanings as those in Figure 1.

DAB, and $C_{12}AC$ in water[21-23] and ~0.003 × 10^{-2} g cm^{-3} for $C_{12}E_7$ in water.[15,17] It lowers for surfactants with longer alkyl chain and with an addition of salt. Therefore, in almost all solutions examined in this work, micelles are present.

The LCST, the UCST, and the upper limit of Krafft boundary are illustrated against salt concentration in Figures 8 and 9. As seen in Figure 9, the LCST of C_nE_7 decreases gradually with an increase in NaCl concentration, similar to results previously reported for homologous species of C_nE_7.[15-17]

Micelles of nonionic surfactant such as oligooxyethylene alkyl ether are hydrated on their surface, forming hydrogen bonds between oxygen atom and water. Hence, nonionic micelles are stably soluble in water at low temperatures. Since micelles release some of hydration water and become less hydrophilic with a rise in temperature, micellar solution separates into two homogeneous solutions. The addition of NaCl promotes the occurrence of phase separation by its salting-out effect. The increase in alkyl chain length increases the hydrophobicity of a surfactant and lowers the LCST.

In Figure 9, the LCST of dimethyloleylamine oxide in water[11] is also drawn. It is very low on account of the high hydrophobicity of this surfactant.

Molecules of ionic surfactant form spherical micelles in

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water. When the salt is added to a micellar solution, intermicellar electrostatic repulsion is reduced and rodlike micelles are often formed above a certain threshold salt concentration.[21,22] The threshold salt concentration for sphere–rod transition is 0.80 and 0.07 M at 25 °C for C_{12}DAC and C_{12}DAB, respectively,[21,22] and 0.06 M at 30 °C for C_{12}AC.[23]

Solutions of C_{12}DAC, C_{12}DAB, and C_{12}AC separate into two-liquid-phases above the salt concentration of 5, 2, and 0.3 M, respectively. The threshold salt concentration for liquid–liquid phase separation is 3–6 times larger than that for sphere–rod transition. This suggests some correlation of the electrostatic shielding effect of salt with phase separation: by the suppression of electrostatic repulsion, the intermicellar attraction increases and, hence, the coagulation of micelles is promoted, thus leading to phase separation.

As seen in Figure 8, the phase separation of alkyldimethylammonium chloride occurs at a lower salt concentration for a surfactant with longer alkyl chain, depending on the hydrophobicity of a surfactant. The threshold salt concentration for phase separation decreases with increasing temperature, because the LCST is observed in temperature–surfactant concentration phase diagram. For C_{16}DAC, the temperature–surfactant concentration phase diagram manifests a closed loop and, therefore, the threshold salt concentration of phase separation rises at a higher temperature.

The lower limit of the threshold salt concentration for phase separation of C_{12}DAB is 2 M at ~35 °C, and solutions with higher salt concentrations exhibit both the LCST and the UCST, reflecting their closed loop profile. The phase separation of C_{12}DAB occurs at salt concentrations lower than that of C_{12}DAC. This is consistent with the salting-out power of anions. The counterion binding on a micelle is more dominant for Br^- than for Cl^-, and thus the effective degree of ionization is less for a micelle of C_{12}DAB than for that of C_{12}DAC. Then a micelle of C_{12}DAB is more hydrophobic than that of C_{12}DAC, and the former solution would separate into two-liquid-phases by the addition of a smaller amount of salt.

On the other hand, the phase behavior of C_{14}DAB seems anomalous, when compared with that of C_{12}DAB or C_{14}DAC. The phase separation of C_{14}DAB occurs at a higher salt concentration than those of C_{12}DAB and C_{14}DAC, inconsistent with the effects of alkyl chain length of surfactant and the salting-out power of salt, both of which enhance the hydrophobicity of micelles.

In order to confirm the validity of the phase behavior observed for C_{14}DAB, the effect of addition of NaBr on a solution of C_{14}DAC was examined. The phase diagram very similar to that for aqueous NaBr solution of C_{14}DAB was obtained with solutions of C_{14}DAC in a presence of 4.3 M NaBr.

Some workers[14–18] have reported the effect of added electrolyte on the phase separation of nonionic surfactants. According to them, simple salts affect phase separation, following the lyotropic series: NaCl depresses the LCST more than NaBr.[15] NaCl destroys hydrogen bonds more readily than NaBr and reduces the hydration on a micelle. We have observed that the addition of sodium salicylate or sodium toluenesulfonate to aqueous $C_{14}E_7$ solutions raises the LCST, despite that organic salts are anticipated to have an especially remarkable binding ability on an ionic micelle, inducing the hydrophobicity of the micelle.

The lyotropic series of anions is more effective in phase separating C_{14}DAB than their salting-out power. This aspect should demonstrate that the miscibility of alkyldimethylammonium halides is based on the hydrogen bonding of surfactant molecule with water.

We have observed that dodecyl-, tetradecyl-, and hexadecyltrimethylammonium chlorides or bromides are miscible between 0 and 100 °C in water even in the presence of NaCl or NaBr up to 4 M. While alkyltrimethylammonium halides cannot hydrogen bond with water, alkyldimethylammonium halides and alkylammonium halides can. The hydrogen bonding of surfactant with water should be one of the most important factors for the liquid–liquid phase separation.

As shown in Figure 8, the threshold salt concentration for phase separation of C_{12}AC increases with an increase in temperature. This is connected with the fact that the LCST might be lower than the freezing point, and, hence, only the UCST is observed. The similar profile with the UCST was reported for zwitterionic surfactants.[20]

It has been recognized in the early years that the occurrence of the lower consolute boundary for aqueous solutions of some solutes is a consequence of the hydrogen bonding between the solute and water at low temperatures.[1] On the other hand, it was reported that micelle molecular weight of oligo(oxyethylene) alkyl ethers in water increased with rising temperature.[1] However, it has also been pointed out that the increase of scattering intensities and hydrodynamic radii accompanying an increase in temperature in the vicinity of the lower boundary for phase separation is not due to micellar growth.[7] Corti et al.[8] have suggested that the phase separation for surfactants with a short alkyl chain, C_6E_3 and C_8E_4, is based on the interaction among small globular micelles, and the miscibility boundary for surfactants with a long alkyl chain, $C_{12}E_8$ and $C_{14}E_7$, may be affected by some micellar growth with temperature besides the intermicellar interaction.

It is likely that the liquid–liquid phase separation of surfactant solutions is induced by the destruction of the specific attractive interaction between the solute and water such as hydrogen bonding, strengthening of the solute–solute attractive interaction, and micellar growth. These factors are affected by the presence of simple salts, in accordance with the lyotropic series and the salting-out power. The influence of added salts is especially drastic for ionic surfactants, owing to their electrostatic shielding and salting-out effects, besides the lyotropic series: the operation of these two mutually opposite effects makes the phase separation behavior of ionic surfactants complicated.

Registry No. C_{12}DAC, 2016-48-0; C_{14}DAC, 2016-47-9; C_{16}DAC, 2016-45-7; C_{12}DAB, 19959-22-9; C_{14}DAB, 64183-88-6; C_{12}AC, 929-73-7; $C_{12}E_7$, 3055-97-8; $C_{14}E_7$, 40036-79-1; $C_{16}E_7$, 4486-31-1; NaCl, 7647-14-5.