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ORIGINAL CONTRIBUTION

M. Miyake
Y. Kakizawa

Study on the interaction between polyelectrolytes and oppositely charged ionic surfactants. Solubilized state of the complexes in the postprecipitation region

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M. Miyake (✉) · Y. Kakizawa
Material Science Research Center
Lion Corporation
Hirai 7-13-12, Edogawa-ku
Tokyo 132-0035, Japan
e-mail: miyamiyu@lion.co.jp
Fax: +81-3-36165376

Abstract The effects of polymer charge and surfactant composition were examined on the complex-precipitation (CP) and phase-separation (PS) regions for cationic cellulose (CC), sodium poly(oxyethylene laurylsulfate) and lauroylamidopropyl-*N*,*N*-dimethylammonioacetate and Na_2SO_4. The solubilized state of the complexes was studied by light scattering in the one-phase, 1ϕ, solution in the postprecipitation region. The cationic charge on the CC and the anionic charge on the surfactant greatly affected the CP and PS regions, to change the domain of the 1ϕ solution. The relative scattering intensity of the complex, $\Delta I_{\mathrm{complex}}$, was high near the CP region and decreased with increasing surfactant and salt concentrations in the 1ϕ solution. The presence of solubilized complexes of polymers cross-linked with surfactant micelles was suggested near the CP region. The cross-linking of the complexes decreased with increasing surfactant and salt concentrations, producing increased micelle binding and charge shielding. The shrinkage of the complexes was considered to bring about the boundary on which $\Delta I_{\mathrm{complex}}$ is equal to the relative scattering intensity of polymer alone in the 1ϕ solutions. Separation of the complexes and the transition of the solution into the PS region were suggested at high concentrations over the boundary.

Keywords Phase behavior · Postprecipitation region · Polyelectrolytes · Surfactants

Introduction

The interaction between polyelectrolytes and ionic surfactants has been extensively studied by many workers, in terms of the phase diagrams, the binding behavior of surfactant ions onto polymer in the preprecipitation region below the critical micelle concentration (cmc), and so on [1–10].

Besides these basic studies, the interaction found many applications in the field of cosmetics and toiletries. In particular, it played an important role in novel shampoo formulations [11–13]. In shampoo, cationic polymer is solubilized in high concentration solutions of anionic surfactants. Its dilution with water in a rinsing cycle, immediately causes precipitation of the complex, thus developing a hair-conditioning action. According to Goddard and Hannan [6], the complex is precipitated because dilution brings the polymer–surfactant composition in to the complex-precipitation (CP) region.

Very few studies were made on the solubilized state of the complex in the postprecipitation region where the surfactant concentration is higher than that in the CP region (above the cmc). This is probably because of the difficulty with which variations in the solubilized state of the complex are observed in the presence of micelles. In addition, there were few systematic works on the phase behavior of the system in the postprecipitation region.

This work aims to clarify (i) the effects of polymer charge and surfactant composition on the phase behavior, and (ii) the solubilized state of the complexes in the postprecipitation region by light scattering methods.

Experimental

Materials

Three kinds of cationic cellulose (CC) were obtained from Lion Co. (Leogarde series). The degree of cationic substitution per unit of glucose (α) was 0.38, 0.21 and 0.10 and the weight-average molecular weights determined by the light scattering was 5.3×10^5, 5.1×10^5 and 5.5×10^5 for the three samples, respectively. The chemical structure of CC is shown in Fig. 1. Sodium poly(oxyethylene laurylether sulfates) [LES, whose average chain length of poly(oxthyethylene) was 3] from Taiko Oil Co. and lauroylamidopropyl-*N*,*N*-dimethylammonioacetate (LPB) from Ippousya Oil Ind. Co. were used without further purification. Sodium sulfate of reagent grade from Tokyo Kasei Ind. Co. was used because it is usually used in shampoo [14]. Distilled water was used in all experiments.

Methods

Phase diagrams

Given amounts of CC, surfactants, salt and water were placed in the test tubes with screwed caps and the contents of the tubes were mixed well at 50 °C. After equilibration for a few days at 25 °C, the sample solutions were checked if there were any precipitates or not.

Light scattering methods

Static light scattering (SLS) and dynamic light scattering (DLS) measurements were performed using a light scattering spectrometer (Photal Co., model DLS-700, 75-mW Ar laser). In SLS, the reduced scattering intensity of the complex ($R_{\theta,\mathrm{complex}}$) is determined theoretically by subtracting the intensity of free surfactant micelles in the bulk ($R_{\theta,\mathrm{free\ micelle}}$) from that of the solution containing polymer, surfactant and salt ($R_{\theta,\mathrm{whole}}$). The scattering intensity of the surfactant solutions without polymer was used as the background [15] since determination of $R_{\theta,\mathrm{free\ micelle}}$ was difficult. The intensity was measured at $\theta = 90°$ because the concentration ranges of polymer and surfactant were so wide that the scattering intensities were beyond the upper detection limits at low angles. The scattering intensity of the solution was expressed as a value, I, relative to that of benzene ($I \equiv I_{90}/I_{90,\mathrm{benzene}}$).

The relative scattered light intensity of the complex, $\Delta I_{\mathrm{complex}}$, is then given by Eq. (1), as shown in Fig. 2.

$$\Delta I_{\mathrm{complex}} = I_{\mathrm{whole}} - I'_{\mathrm{micelle}} \qquad (1)$$

where I_{whole} is the relative scattering intensity of the solution and I'_{micelle} is that of the solution containing surfactant and salt alone.

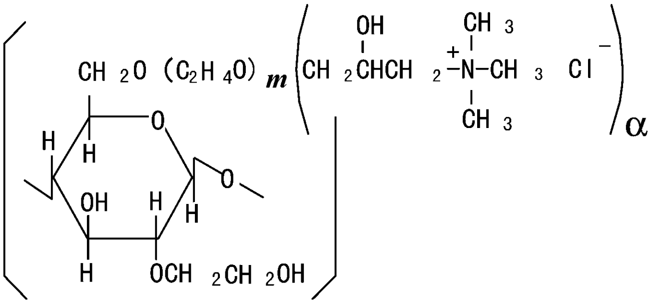


Fig. 1 Chemical structure of cationic cellulose. $m = 2$–3 and α is the degree of cationic substitution

Although the scattering intensity of the micelles bound to the polymer is ignored, $\Delta I_{\mathrm{complex}}$ refers to the conformation of the polymer chains in the complex. Changes in the solubilized state of complex were conducted through comparison of $\Delta I_{\mathrm{complex}}$ of the solutions with the relative scattering intensity, I_{polymer}, for solutions containing 0.1% (w/w) CC and salt at the same concentrations as those in sample solutions.

DLS measurements were also carried out at $\theta = 90°$. The Stokes diameter of the complex, d, was determined by Eq. (2).

$$d = k_{\mathrm{B}}T/3\pi\eta D \ , \qquad (2)$$

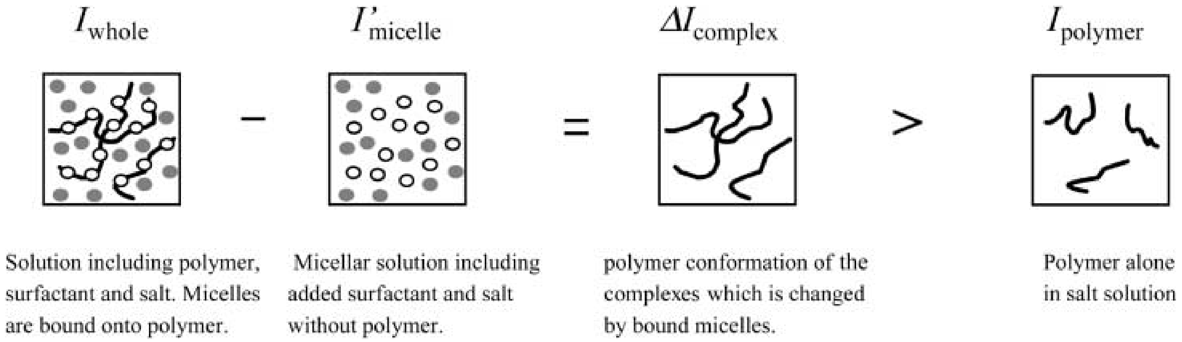
where D is the translational diffusion constant of the solute, k_{B} is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent. The apparent size, d_{app}, was larger than the size of the micelles owing to the complex formation.

Results and discussion

Phase behavior

Phase diagrams of systems containing 0.1% (w/w) CC and varying concentrations of surfactants, LES and LPB, and salt, Na_2SO_4, are shown in Fig. 3. Two regions appeared in each phase diagram: one was the CP region where the complex is precipitated owing to charge neutralization, and the other was the phase-separation (PS) region in which insoluble matter different from the complex is dispersed in solutions at high surfactant and salt concentrations. The two regions were distinguished

Fig. 2 Relative scattering intensity of the polymer in the complexes



visually. The precipitated complex was observed at the bottom of the test tube with clear supernatant solution in the CP region, whereas the solution was turbid in the PS region.

In the case of LES, the CP region broadened with increasing degree of cationic substitution of CC, α. It was connected to the PS region on the high-salt-concentration side at $\alpha = 0.38$ for CC, while a clear one-phase, 1ϕ, solution appeared in the same region for CC with $\alpha = 0.21$ and 0.10 (Fig. 3a–c).

When the ratio LES/LPB decreased, the CP region shifted slightly toward the lower-concentration side of the surfactants and the salt, while the PS region shifted toward the lower-concentration side of the surfactants and the higher-concentration side of the salt (Fig. 3b, d, e). The above findings indicate that domain of the 1ϕ solution can be altered by adjusting the charges on polymer and surfactant.

Light scattering measurements

The effect of the surfactant concentration on the solubilized state of the complexes was examined first in the 1ϕ solution at $\alpha = 0.21$ for CC and a surfactant composition of LES/LPB = 3/1 (w/w) (Fig. 3d). The relative scattering intensity of the complex, $\Delta I_{\mathrm{complex}}$, was measured at Na_2SO_4 concentrations of 0.3, 1.0 and 3.0% (w/w) (Fig. 4a–c). DLS measurements were also

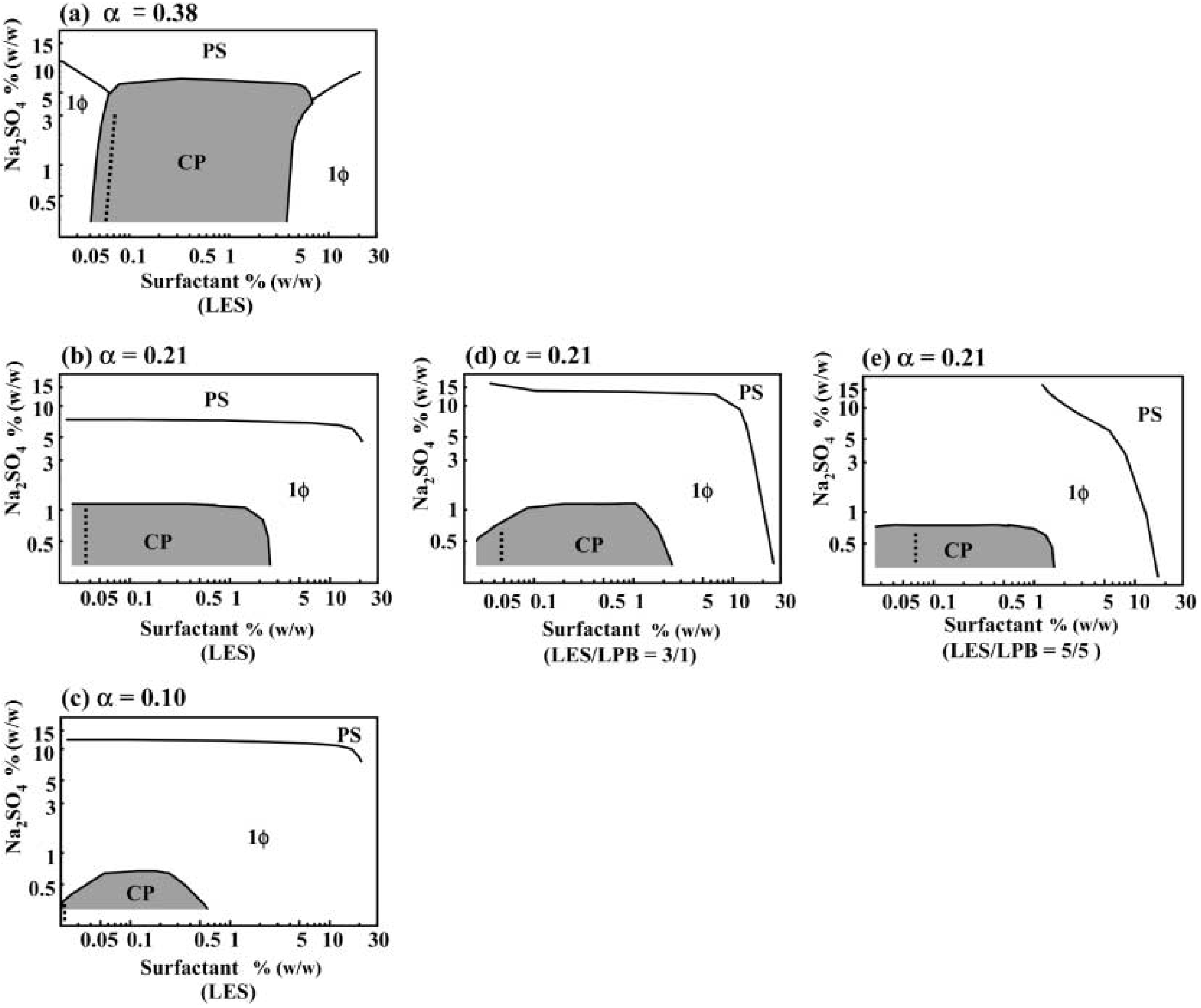


Fig. 3a–e Partial phase diagrams for systems containing CC at 0.1% (w/w), sodium poly(oxyethylene laurylsulfate) (*LES*) and lauroylamidopropyl-*N*,*N*-dimethylammonioacetate (*LPB*) and Na_2SO_4. **a, b, c**: LES, degrees of cationic substitution $\alpha = 0.38$, 0.21 and 0.10. **d, e**: mixtures of LES and LPB at $\alpha = 0.21$. (complex-precipitation region: *CP*, phase-separation region: *PS*, clear one-phase solution region: *1ϕ*). *Dotted lines* in the CP region indicate a 1:1 molar ratio of cationic groups to LES

performed under the same conditions as above to determine the apparent size, d_{app} (Fig. 4d–f).

At 0.3 and 1.0% (w/w) Na_2SO_4, $\Delta I_{complex}$ was much larger than $I_{polymer}$ near the CP region and then decreased with increasing surfactant concentration, converging to the same level as $I_{polymer}$. The apparent size, d_{app}, for the corresponding solution was also much larger than the micellar size, d_{mic}, near the CP region because of complex formation, and then it decreased as the surfactant concentration increased, finally approaching the same level as d_{mic}.

Goddard and Leung [16], Guillemet and Piculell [17] and Hoffmann et al. [18] showed that the viscosity of a solution in CC and sodium dodecyl sulfate systems increased near the CP region. Magny et al. [19, 20] and Biggs et al. [21] reported that, in solutions of surfactant and hydrophobically modified water-soluble polymer, mixed micelles consisting of molecules of the surfactant and hydrophobic groups of the polymer are formed around the cmc. They cross-linked between polymers to cause gelation or thickening. The viscosity of the 1ϕ solution of our sample also showed a remarkable increase around the CP region. In view of these findings, very high values of $\Delta I_{complex}$ and d_{app} would imply formation of a structure composed of polymers cross-linked through micelles. If the number of micelles to bind is not large enough to all polymer molecules, cross-linking would be enhanced. Increasing micelles bound on to the polymer with increasing surfactant concentrations would increase the electrostatic repulsion between polymer-bound micelles. This would then lead to a breakdown of the cross-linkage between polymers and $\Delta I_{complex}$ decrease (Fig. 4a, b).

Next, the effect of salt concentration on the solubilized state of the complexes was examined. With increasing salt concentration, $\Delta I_{complex}$ decreased at a surfactant concentration of 3% (w/w) and approached the level of $I_{polymer}$ (Fig. 5). At 3.0% (w/w) Na_2SO_4, $\Delta I_{complex}$ was almost the same as $I_{polymer}$ at all surfactant concentrations (Fig. 4c). This indicates that increasing ionic strength disrupts the micelle-mediated cross-linkages between the polymers. The increased ionic strength shields the electrostatic interaction between the polymers and the micelles, and weakens the cross-linkage.

McQuigg et al. [22] and Xia et al. [23] reported that high salt concentrations prevent micelles composed of anionic and nonionic surfactants from binding to the poly(dimethyldiallylammonium chloride).

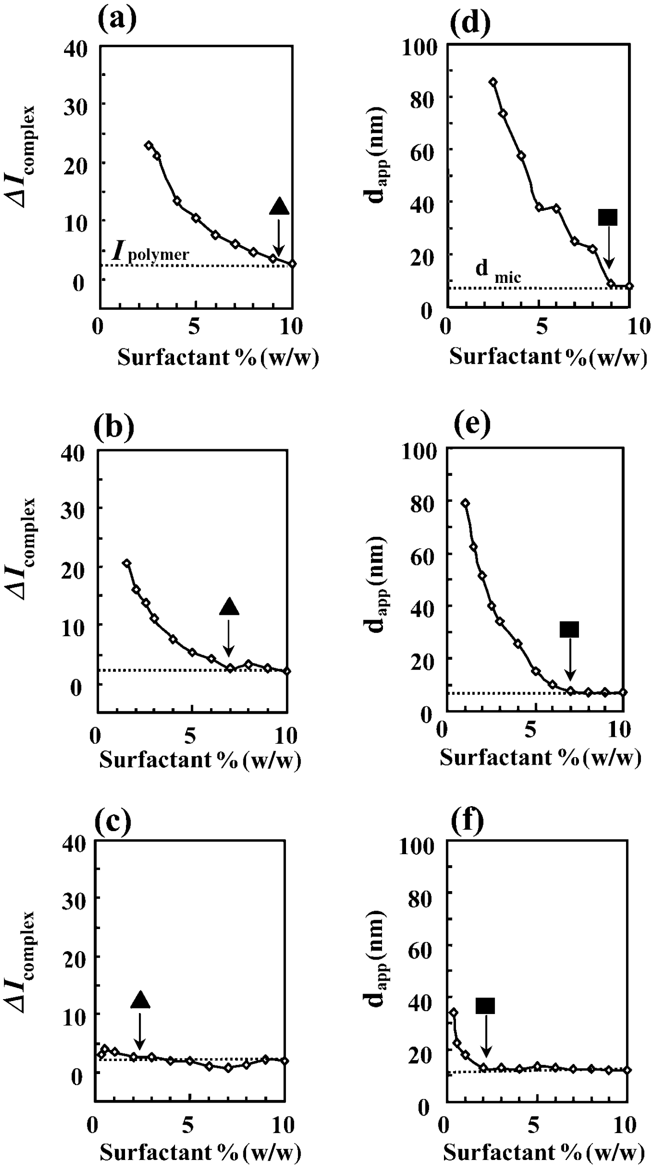


Fig. 4a–f Relative scattered intensity and apparent particle size of the solubilized complexes in 1ϕ solutions at $\alpha = 0.21$ and LES/LPB = 3/1. The salt concentrations are 0.3% (w/w) in **a** and **d**, 1.0% (w/w) in **b** and **e** and 3.0% (w/w) in **c** and **f**, respectively

Complex formation in the postprecipitation region

Figure 6 gives those surfactant concentrations which correspond to $\Delta I_{complex} = I_{polymer}$ (indicated by full triangles) in the 1ϕ solution at $\alpha = 0.21$ for CC and the LES/LPB ratio of 3/1 (w/w). The line passing through these triangles encircles the CP region. The boundary thus obtained nearly coincided with that encircled with full squares, in which d_{app} is equal to d_{mic} (Fig. 4d–f). The state of the complexes on this boundary is supposed as follows.

At salt concentrations of 0.3 and 1.0% (w/w), the polymer chain conformation of the complex would be more extended than that of the polymer alone, if the micellar binding through hydrophobic interaction is assumed to be saturated (even if no data are available on the binding amount of surfactant). Contrary to this expectation, $\Delta I_{complex}$ was almost identical with $I_{polymer}$

at high surfactant concentrations. The cause is that the micelles increased in the bulk, and they acted in shielding the repulsion between the cationic charges of the polymer, thereby causing the complex to shrink. The finding that d_{app} is very close to d_{mic} may have the same reason.

An increase in the salt concentration increased shielding of the charges of the polymer and micelles and changes the solubilized state of the complexes cross-linked by micelles (Fig. 5). Hayakawa and Kwak [1] found that an increase in the salt concentration decreases the binding constant and the cooperativity parameter of dodecyltrimethylammonium ions to sodium dextran sulfate and sodium poly(styrene sulfonate). Kiefer et al. [24] reported that the plateau value of the degree of binding degree of tetradecyltrimetylammonium ions to poly(acrylic acid) (PAA) decreases though the degree of dissociation of PAA is increased in the presence of salt. These findings suggest a competitive binding of salt and surfactant ions onto the polymer. WE suppose that the competitive interaction of the salt increased shielding of the charges of the polymer and micelles in the postprecipitation. It would prevent the complex from forming so many cross-links at the high salt concentrations.

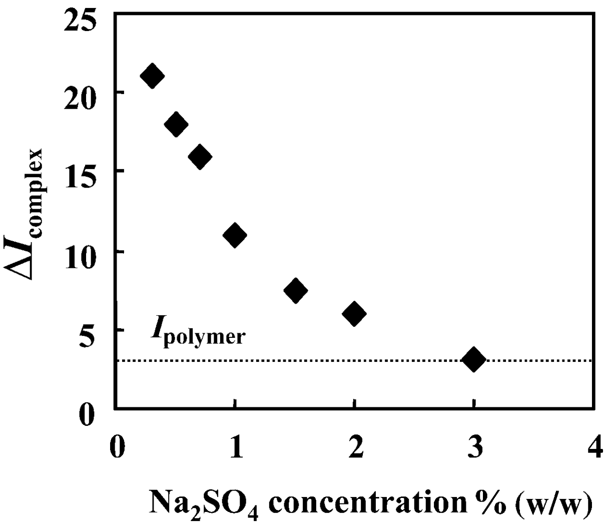


Fig. 5 Effect of salt concentration on $\Delta I_{\mathrm{complex}}$ at a surfactant concentration of 3% (w/w)

At 3% (w/w) salt, $\Delta I_{\mathrm{complex}}$ was almost the same as I_{polymer}, which didn't depend on the surfactant concentration (Fig. 4c). This reason may be that the polymer conformation of the complex shrinks by the salt, in addition the complexes have few cross-links. This is supported by the fact that the square root of the radius of gyration for CC with $\alpha = 0.21$ changes from 193 nm (random coil) in pure water to 68 nm (rodlike) in 3% (w/w) salt solution.

Furthermore, $\Delta I_{\mathrm{complex}}$ and d_{app} increased again near the PS region (data not shown) in the 1ϕ solutions. This suggests that separation of the complexes occur and the solution transforms into the PS region.

In conclusion, the boundary of the 1ϕ solution indicates the change of the state of the solubilized complexes. Thus, phase separation gradually take place and the solution transforms into the PS region, when the surfactant and salt concentrations increase over the boundary.

Conclusions

The degree of cationic substitution of CC and the charge of the surfactant affected the CP and the PS regions, and produced changes in the composition of the 1ϕ solution in the postprecipitation region.

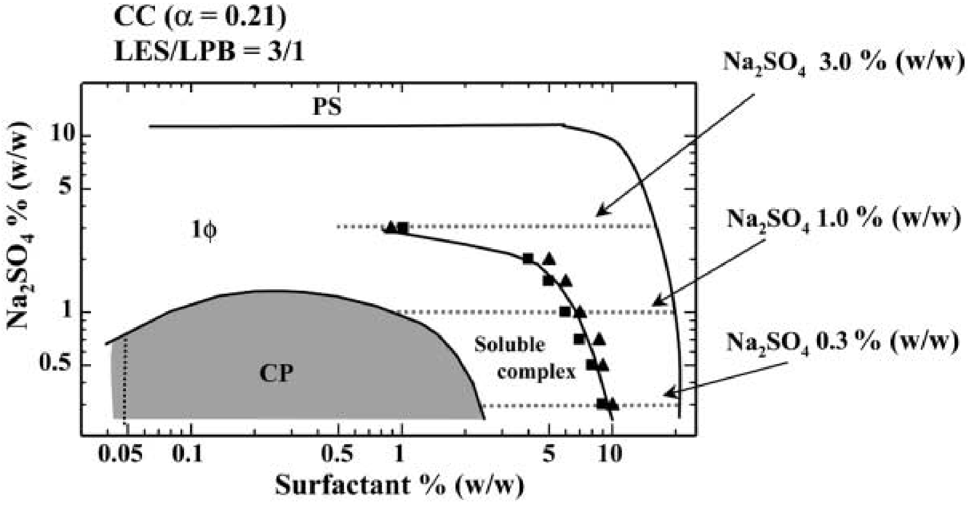


Fig. 6 Boundary on which the solubilized state of the complexes significantly changes in the 1ϕ solution of the post-precipitation region

Large solubilized complexes consisting of polymers cross-linked through micelles were observed in the 1ϕ solution near the CP region. An increase in the surfactant concentration decomposed cross-links and small complexes were formed. High concentrations of salt weakened the electrostatic interaction between the binding sites on the polymer and the micelles and reduced the size of the complexes.

The presence of a boundary on which $\Delta I_{\mathrm{complex}} = I_{\mathrm{polymer}}$ was found in the 1ϕ solution on the higher-concentration sides of the surfactant and the salt. The reason may be shrinkage of the polymer conformation of the complex brought about by coexisting free micelles and salt ions in the bulk solution. The solubilized complexes gradually separated from the solution outside this boundary.

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