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

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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-$\text{N,}\text{N}$-dimethylammoniocetate and Na$_2$SO$_4$. The solubilized state of the complexes was studied by light scattering in the one-phase, $1\phi$, 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 $1\phi$ solution. The relative scattering intensity of the complex, $\Delta I_{\text{complex}}$, was high near the CP region and decreased with increasing surfactant and salt concentrations in the $1\phi$ 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 $\Delta I_{\text{complex}}$ is equal to the relative scattering intensity of polymer alone in the $1\phi$ 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 into 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. (Leoger series). The degree of cationic substitution per unit of glucose (x) was 0.38, 0.21 and 0.10 and the weight-average molecular weights determined by the light scattering was $5.3 \times 10^5$, $5.1 \times 10^5$ and $5.5 \times 10^5$ for the three samples, respectively. The chemical structure of CC is shown in Fig. 1. Sodium poly(oxyethylene lauryl ether sulfates) [LES, whose average chain length of poly(oxyethylene) was 3] from Taiko Oil Co. and lauroylamidopropyl-N,N-dimethylammonioacetate (LPB) from Ippouya 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 (Photol Co., model DLS-700, 75-mW Ar laser). In SLS, the reduced scattering intensity of the complex ($R_{\theta,\text{complex}}$) is determined theoretically by subtracting the intensity of free surfactant micelles in the bulk ($R_{\theta,\text{free,micelle}}$) from that of the solution containing polymer, surfactant and salt ($R_{\theta,\text{whole}}$). The scattering intensity of the surfactant solutions without polymer was used as the background [15] since determination of $R_{\theta,\text{free,micelle}}$ was difficult. The intensity was measured at $\theta = 90^\circ$ 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 ($I = I_{\text{rel,benzene}}$).

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

$$\Delta I_{\text{complex}} = I_{\text{whole}} - I_{\text{micelle}}$$  \hspace{2cm} (1)

where $I_{\text{whole}}$ is the relative scattering intensity of the solution and $I_{\text{micelle}}$ is that of the solution containing surfactant and salt alone.

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$_2$SO$_4$, 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. 1 Chemical structure of cationic cellulose, $m = 2-3$ and $z$ is the degree of cationic substitution

Although the scattering intensity of the micelles bound to the polymer is ignored, $\Delta I_{\text{complex}}$ refers to the conformation of the polymer chains in the complex. Changes in the solubilized state of complex were conducted through comparison of $\Delta I_{\text{complex}}$ of the solutions with the relative scattering intensity, $I_{\text{polymer}}$, 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 $\theta = 90^\circ$. The Stokes diameter of the complex, $d$, was determined by Eq. (2).

$$d = k_B T/3\pi \eta D$$  \hspace{2cm} (2)

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