Coacervation in Cationic Polyelectrolyte Solutions with Anionic Amino Acid Surfactants

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Abstract: Coacervates formed by cationic polyelectrolytes and anionic surfactants are utilized to improve the user’s tactile perception of shampooing hair during washing and after drying. In this study, we investigated the formation and structure of coacervates in aqueous systems containing anionic amino acid surfactants. The phase behaviors at constant temperature were investigated in aqueous systems combining cationic polyelectrolyte JR-400 with potassium cocoyl glutamate (CoGluK) or potassium cocoyl glycinate (CoGlyK) for a qualitative depiction of coacervate formation. The composition range of coacervate formation varied with the hydrophilic group of the surfactant. The surface tension was measured at different surfactant concentrations and constant polyelectrolyte concentration. The surface tension behavior revealed the critical association concentrations and critical micelle concentrations, indicating that coacervate was produced via complex formation through electrostatic interaction between opposite charges. Optical microscopy and small-angle X-ray scattering measurements revealed that the coacervates were composed of fibrous aggregates, a few microns thick, and those formed in the CoGlyK system had thicker fibers.

Key words: coacervation, polymer-surfactant interaction, amino acid surfactant, phase behavior, small-angle X-ray scattering

1 Introduction

When an ionic surfactant and a polyelectrolyte with opposite charges are mixed in an appropriate ratio, precipitation may occur as a complex coacervation. Fundamental investigations in the fields of solution chemistry and colloid chemistry focused on such complex coacervation (hereafter simply referred to as coacervation) have long been reported. The phase behavior in ternary water/surfactant/polyelectrolyte systems is well understood1, and the effects of various parameters, such as charge densities of surfactant micelles and polyelectrolytes, molecular weights of polymers, surfactant/polymer mixing ratio, and concentration, on coacervate formation have been reported2-3. The molecular mechanism of coacervation formation4 has additionally been clarified.

Hair shampoos often contain a cationic polyelectrolyte and an anionic surfactant. Such a combination of oppositely charged molecules leads to coacervate formation during rinsing in the process of hair washing. The coacervate generated adheres to the hair surfaces, thereby providing a lubricating effect5-6 and promoting the adhesion of the functional substances in shampoo, such as silicone oil, to hair7-9. It is known to improve the user’s tactile perception while washing and after drying hair. Cellulose derivatives have long been used as cationic polyelectrolytes in shampoos. High-performance and low-cost alkyl sulfate salts or alkyl sulfate ester salts are widely used as anionic surfactants. However, there are concerns about the use of such petroleum-based surfactants from the perspectives of skin irritation and environmental impact.

Acyl amino acid salts, which consist of fatty acids and various amino acids, have high biodegradability and are, therefore, considered environment-friendly green surfactants. They are mainly used in cosmetics as they cause low skin irritation. In particular, anionic acyl glutamate and glycinate salts have been used in various cosmetics, and there is a vast literature on the dissolution states of, and molecular assembly formation in, aqueous solutions10-18. However, no studies on coacervation in combination with cationic polyelectrolytes have been reported yet. In the
present study, therefore, the amino acid surfactants, i.e., potassium cocoyl glutamate (CoGluK) or potassium cocoyl glycinate (CoGlyK), were separately combined with the cationic polyelectrolyte, JR-400, in which a substituent containing a quaternary ammonium salt was grafted to a cellulose chain. The formation and structure of coacervates were investigated in the different aqueous systems.

2 Experimental
2.1 Materials
A cationically modified cellulose ether, JR-400 (Dow Chemical, USA), was used. Its molecular structure is illustrated in ref. 21. Its molecular weight, degree of substitution, and charge density were approximately 500000 g mol$^{-1}$, 0.27, and 1000 g mol$^{-1}$, respectively$^{19,21}$. CoGlyK and CoGluK were obtained from Ajinomoto Co., Inc. (Japan). The degree of carboxylic acid neutralization is 1 for CoGlyK and CoGluK, and their typical molecular structures are shown in Fig. 1. The carbon number $n$ in the cocoyl group varied in the range 7–17, and the average $n$ was 11.3$^{22}$. Deionized water, obtained from an Elix 3 (Nihon Millipore) water purification system, was used as the solvent.

2.2 Sample preparation
A predetermined composition of reagents was weighed, placed in a 20 mL screw-capped bottle, and uniformly mixed using a vortex mixer or magnetic stirrer or shaker. The sample compositions, $W_P$ and $W_S$, were determined using Equations (1) and (2), respectively.

\begin{align*}
W_P &= P/(S + P), \quad (1) \\
W_S &= (S + P)/(W + S + P), \quad (2)
\end{align*}

where $S$, $P$, and $W$ indicate the mass of surfactant, polyelectrolyte, and water, respectively.

2.3 Visual observation
The samples prepared were placed in an incubator set at 25°C for several hours to several days, and the presence or absence of coacervate was visually observed.

2.4 Optical microscopy
A differential interference microscope (CX31-P, Olympus, Japan) was used to perform simple polarization observations at room temperature ($25 \pm 5$°C).

2.5 Conductivity measurement
A total of 25 g of water was taken in a 50 mL glass container, and the mother liquor (1.41 wt.% surfactant aqueous solution) was added with a micropipette to adjust the concentration of the solution. The temperature of the solution was set at 25°C using a constant-temperature water bath, and the electrical conductivity at each concentration was measured using an electrical conductivity measuring device (DS-72, Horiba, Japan) and an electrical conductivity cell (3552-10D, cell constant of 0.976 cm$^{-1}$).

2.6 Surface tension measurement
The surface tension was measured using the Wilhelmy method (K100, Krüss, Germany). The plate used was a roughened platinum plate designed for K100.

2.7 Small- and wide-angle X-ray scattering (SWAXS)
A small-angle X-ray scattering (SAXS) device (SAXSess, Anton Paar, Austria) was used. The X-rays (Cu-Kα, wavelength $\lambda = 0.1542$ nm) used to irradiate the samples were generated by a sealed glass X-ray tube and collimated by a block optical system. A glass capillary sample cell (1 mm sample thickness) was used. The scattered X-rays were detected by an image plate, which was read using Cyclone (Perkin Elmer, USA) and a 1D spectrum was obtained using SAXSquant software (Anton Paar, Austria). The measurements were performed by setting the parameters of the X-ray generator at 40 kV and 50 mA. The X-ray irradiation time was 10 min.

3 Results and Discussion
3.1 Phase behavior
Figure 2 shows the partial phase diagrams of the water/
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Fig. 2  Phase diagrams of (a) water/CoGlyK/JR-400 system, and (b) water/CoGluK/JR-400 system at 25°C. Shaded areas indicate coacervation regions.

In both the systems, the coacervation region was formed when the polyelectrolyte and surfactant were mixed, and furthermore, the coacervates were formed from high to low solute concentrations. In addition, the coacervation region exists around the charge neutralization compositions that is approximately calculated as mass ratios, 33/67 and 41/59 in the CoGlyK system and CoGluK systems, respectively. Such phase behavior is also observed in other systems composed of cationic cellulose and anionic surfactant. In the coacervation region, the samples are in a two-phase equilibrium of an extremely diluted aqueous solution phase and the coacervate phase. Therefore, the tie line in the coacervate region (two-phase equilibrium region) connects the composition near the water apex of the phase diagram with a solute-rich composition. The composition range of coacervate formation at a constant solute concentration (constant \( W_s \)) is almost unchanged in the CoGlyK system regardless of the solute concentration. On the other hand, in the CoGluK system, the composition range of coacervate formation depends on the solute concentration and especially extends to the surfactant-excess composition in the diluted region. A general commercial shampoo has an excess of surfactant relative to the polyelectrolyte; for instance, \( W_s = 0.0625 \) in a previously published work. Considering the composition change, which occurs during the process of rinsing in shampooing, as a model for shampoo formulation (\( W_s = 0.1 \) and \( W_p = 0.0625 \)), the solution state changes as shown in Table 1. Coacervates are formed in the CoGluK system but not in the CoGlyK system, indicating that the former is more suitable for use in shampoos.

Coacervate formation was not influenced by temperature in either system when the composition range of coacervate formation at \( W_s = 0.01 \) was investigated in the temperature

![Fig. 2](image-url)

**Table 1** State of dilution.

| S + P [wt. %] | 10 | 7.5 | 5 | 2.5 | 1 |
|---------------|----|-----|---|-----|---|
| CoGlyK        | T  | T   | T | T   | T |
| CoGluK        | T  | T   | T | C   | C |

T: Transparent, C: Coacervation.

![Fig. 3](image-url)

Optical micrographs of coacervate in (a) CoGlyK, and (b) CoGluK systems at \( W_s = 0.01 \) and \( W_p = 0.6 \).
range 5–55°C.

Figure 3 shows the optical micrographs of the coacervates. In both systems, fibers, which are a few microns thick, form a network structure. The formation of fibers suggests that the polymer chains are oriented in a 1D direction to some extent. Thicker fibers are observed in the CoGlyK system than in the CoGluK system.

3.2 Adsorption behavior

Figure 4 shows the results of the surface tension measurements of the CoGlyK and CoGluK aqueous solutions, and of each surfactant aqueous solution with the coexistence of 0.1 wt.% JR-400 at 25°C. In the aqueous solutions of CoGlyK and CoGluK, the surface tension decreases with increase in concentration and becomes constant at CMC. The CMC values are shown in Table 2. The CoGlyK system without the polymer has a slightly higher CMC value than the CoGluK system although the difference cannot be straightforwardly interpreted since the averaged chain lengths and those distribution in the hydrophobic part of those surfactants are not accurately controlled. In the presence of the polyelectrolyte, the surface tension curves exhibit two plateau regions. This is the adsorption behavior generally seen in a polyelectrolyte-surfactant mixed system with opposite charges\(^1\). At the lower inflection point, the surfactant electrostatically initiates binding to the polymer and this concentration is the critical association concentration (CAC). The other inflection point is the concentration after which surfactant micelles start to form (CMC with the presence of polymer)\(^1\), similar to that found in each solution with the surfactant alone. The CMCs were higher in the systems with the polymer and the gap in the CoGluK systems is obviously larger than that in the CoGlyK systems, suggesting larger adsorption amount of CoGluK to the polymer than that of CoGlyK. As the CoGlyK and CoGluK systems exhibit the typical behavior of oppositely charged polymer-surfactant systems, the coacervation in both the systems can be considered complex coacervation.

3.3 SAXS

The SAXS measurements were performed to investigate the microscopic structure of the coacervate, and the results are shown in Fig. 5. A SAXS spectrum is influenced by fluctuations in the sample electron density in the range of several nm to several tens of nm. In the systems in this work, coherent scattering from micelles was mainly observed. In the case of the coacervate samples (Fig. 5(a)–(d)), a broad peak was seen at approximately \(q = 1.3 \text{ nm}^{-1}\).
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4 Conclusion

In this study, we mainly investigated the effect of amino acid groups on coacervate formation in mixed aqueous systems of anionic amino acid surfactant and cationic polyelectrolyte. The solution state was examined by changing the mixing compositions of the amino acid surfactants, i.e., CoGluK or CoGlyK, and cationic cellulose JR-400, as well as the solute concentration. Coacervate formation was confirmed in both the systems. The CoGluK system was likely to form coacervates upon dilution at excess surfactant composition. The surface tension measurements revealed that coacervate was formed owing to the formation of a complex of cationized cellulose and surfactant. Observations using an optical microscope revealed that the microscopic structures of the coacervates had fiber-like shapes with thicknesses of several microns. The SAXS results suggested that the polymer network density in the coacervates was higher in the CoGlyK system than that in the CoGluK system unless microscopic phase separation occurs. This could explain the thicker fibers in the coacervate in the CoGlyK system, as shown in Fig. 3, because of the stronger hydrogen bonding in its denser polymer network.

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