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Recent progress of the characterization of oppositely charged polymer/surfactant complex in dilution deposition system

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ABSTRACT

A mixture of oppositely charged polymer and surfactants changes the solubilized state, having a complex precipitation region at the composition of electric neutralization. This complex behavior has been applied to surface modification in the fields of health care and cosmetic products such as conditioning shampoos, as a dilution-deposition system in which the polymer/surfactant mixture at the higher surfactant concentration precipitates the insoluble complex by dilution. A large number of studies over many years have revealed the basic coacervation behavior and physicochemical properties of complexes. However, the mechanism by which a precipitated complex performs surface modification is not well understood. The precipitation region and the morphology of precipitated complex that are changed by molecular structure and additives affect the performance. Hydrophilic groups such as the EO unit in polymers and surfactants, the mixing of nonionic or amphoteric surfactant and nonionic polymer, and the addition of low polar solvent influence the complex precipitation region. Furthermore, the morphology of precipitated complex is formed by crosslinking and aggregating among polymers in the dilution process, and characterizes the performance of products. The polymer chain density in precipitated complex is determined by the charges of both the polymer and surfactant micelle and the conformation of polymer. As a result, the morphology of precipitated complexes is changed from a closely packed film to looser meshes, and/or to small particles, and it is possible for the morphology to control the rheological properties and the amount of adsorbed silicone. In the future, further investigation of the relationships between the morphology and performance is needed.

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1. Introduction

The mixtures of oppositely charged polymer and surfactant are complex and interesting systems because the polymer/surfactant complex forms various states such as liquid, gel and solid by their molecular structure and composition. Such complexes are exceedingly important because they have been applied in industrial fields to produce many products such as cosmetics, medicines, and foods.

The oppositely charged polymer/surfactant complex changes its dissolved state by the electric equivalent ratio (S/P), in which P is the number of ionized groups of polymer and S is the number of ionized groups of surfactant, and has three different stages [1,2] (Fig. 1). The first stage (Stage 1) is $S/P < 1$ at the surfactant concentration below cmc, where surfactant ions cooperatively bind to the polymer. The complex solution is a single phase and the complex still has the polymer's charge. The onset of the second stage (Stage 2) is led by electric neutralization, $S/P = 1$, and the complex becomes insoluble and precipitates. As the surfactant concentration increases, micelles are gradually formed on the precipitated complex ($S/P > 1$), and the complex is finally resolubilized and coexists with free micelles in Stage 3. As the composition changes from Stage 1 to Stage 3, the charge of the polymer/surfactant complex is converted from the polymer charge to the bound micelle charge [3]. Stage 2 has been called the complex precipitation region.

The complex precipitation behavior offers many benefits for the development of conditioning shampoo [4–6]. Typical formulations of shampoo are including anionic, amphoteric and nonionic surfactants as detergents, and cationic polymer as a conditioning agent to enhance aesthetics [6,7]. Shampoo in the bottle is a mixture of Stage 3. The cationic polymer is solubilized by anionic and other surfactant micelles, and the mixture is then diluted by water in the washing and rinsing process. Thereby, the surfactant concentration of Stage 3 decreases to that of Stage 2, and the polymer/surfactant complex is precipitated. Nowadays, this complex precipitation has become the key technology of shampoo since the dilution-deposition system was proposed by Goddard et al. [8]. The precipitated complex promotes foaming [9–11], friction reduction of the hair surface [12,13] and adsorption of colloid particles like silicone emulsion [13–15], and has a great influence on the hair feel that consumers can recognize [14,16,17].

For over 30 years since the use of complex precipitation was started, many kinds of polymer/surfactant systems have been studied by various approaches. In the early period of these studies, much research was done on the cooperative binding process [18,19] and the phase behavior that appear in the complex precipitation region [20]. Furthermore, we have deepened our understanding of the physicochemical properties of the polymer/surfactant system by tensiometry, turbidimetry, and/or calorimetry, and the dissolved state of complex in bulk by dynamic light scattering (DLS) and Electrophoretic light scattering (ELS), and the adsorbed state at air–liquid and solid–liquid interfaces by X-ray photoelectron spectroscopy (XPS), X-ray reflectometry (XRR), ellipsometry or atomic force microscopy (AFM) [21–24]. Recently, a robotic combinational technique, high throughput screening, has applied to characterize and optimize products that depend on complex coacervation formation in formulation science [25]. The nonequilibrium adsorbed state of complex at the air–liquid interface has been directly observed by Brewster angle microscopy (BAM) and neutron reflectometry (NR) [26]. Sustained research by Dubin et al. on complex formation and precipitation have yielded many suggestions regarding the dilution-deposition system. They studied the interaction between polymer and surfactant micelles in Stage 3, and the many factors that decide the complex precipitation behavior. The factors were related with the charges of polymer and surfactant micelle [27–29], the ion strength by salt [30,31] the molecular weight and the amount of polymer [32–35], the flexibility of polymer chain [36], and temperature and shear [37–39] that induce coacervation. In their studies, poly (diallyldimethylammonium chloride) (PDADMAC) and a mixture of sodium dodecyl sulfate (SDS) and nonionic Triton X-100 were mainly used.

On the other hand, the natural-based cationic hydroxyethylcellulose (Cat-HEC) and cationic guar gum (Cat-Guar) [13,40], and the synthetic copolymer with acrylamide and diallyldimethylammonium (PQ-7) [41] are now commonly used. Many novel synthetic polymers have been developed, expanding the application of precipitated complex [42]. Moreover, lauryl ethoxylate sulfate (LES) is used as an anionic surfactant. Many other nonionic, amphoteric, and/or amino acid based surfactants are combined to tune the complex precipitation behavior. One indicator of good performance for shampoo is that the precipitation starts at a lower dilution ratio and takes place over a wider dilution ratio [25]. However, it is occasionally reported that the SDS, that has been used in basic studies as an anionic surfactant, narrowed the complex precipitation region by dilution [14]. It is not fully understood why SDS does not have a good influence in the complex precipitation region. In this way, even with widely-used ingredients, the mechanism of precipitation by dilution and the relationships between the precipitated complex and the performance are not well understood, with slight differences in the molecular structure and the combination of polymers and surfactants. One reason would be that the concentration of multiple components is reduced suddenly in the dilution process. Another reason is that minute quantities of nonequilibrium precipitated complex affect the performance. We can presume that the morphology of precipitated complex and its rheological properties greatly affect the performance, but it is difficult to investigate them in detail. The goal of the dilution-deposition system in applications is to find how to control the morphology of the complex as desired and to produce excellent

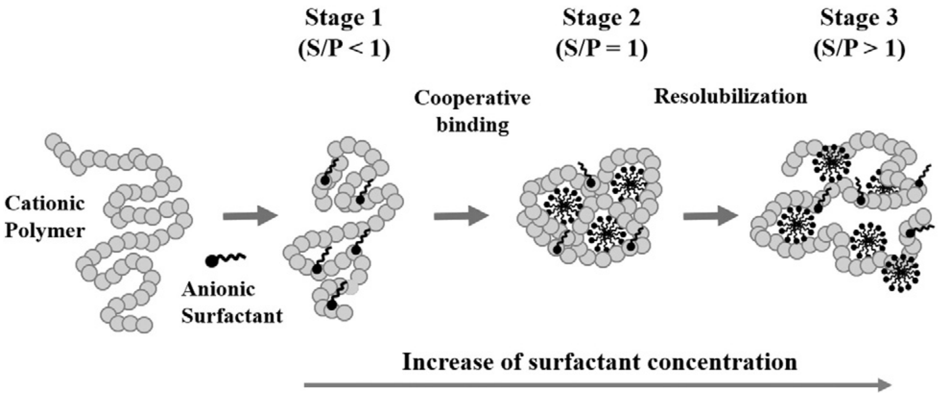

Fig. 1. Schematic representation of the three dissolved states of oppositely charged polymer/surfactant complex in solution. Stage 1 and Stage 3 are clear one-phase solutions, Stage 2 is turbid due to insoluble precipitated complex.
Images taken from ref. [24].