



A pseudo-quantitative ternary surfactant ion mixing plane phase diagram for a cationic hydroxyethyl cellulose with dodecyl sulfate counterion complex salt



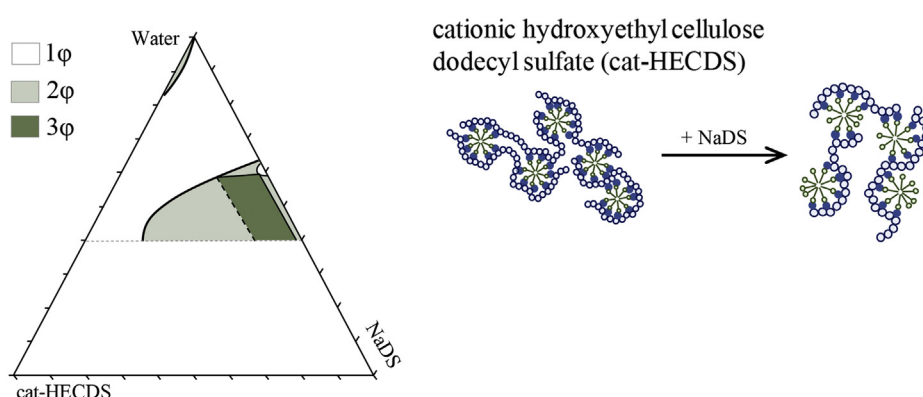
Nada H. Baalbaki*, Gerald B. Kasting

James L. Winkle College of Pharmacy, University of Cincinnati Academic Health Center, Cincinnati, OH 45267, USA

HIGHLIGHTS

- The phases and structures of Polyquaternium-10 complex coacervate were determined.
- The surfactant ion mixing plane phase diagram was built for the complex coacervate.
- This phase diagram was compared to the phase diagram made with a similar polymer.
- The polymer's degree of charge substitution altered the diagram's phase boundaries.
- The coacervate's anion to cation molar ratio determined location of the boundaries.

GRAPHICAL ABSTRACT



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ABSTRACT

The surfactant ion mixing plane phase diagram was constructed for cationic hydroxyethyl cellulose dodecyl sulfate (cat-HECDS), sodium dodecyl sulfate (NaDS) and water. The number of phases and structures present in the prepared ternary composition were assessed visually and guided the placement of phase boundaries. Two multi-phase regions surround a large, central one-phase isotropic region. In the dilute portion of the diagram, an isotropic-isotropic two-phase region exists along the water-complex salt axis. A concentrated multi-phase region adjacent to the water-NaDS axis includes a three-phase region defined as isotropic-hexagonal-monoclinic surrounded by three two-phase regions of isotropic-monoclinic, isotropic-hexagonal, and hexagonal-monoclinic.

This phase diagram is similar to one previously published in this journal [Svensson et al., *Colloids Surf. A*, 228 (2003) 91–106]. Here the degree of cationic substitution on the polymer was reduced by half. This resulted in a shift in the locations of the phase boundaries, but not the phases and structures, present in this plane. Evaluating the phase boundaries as a function of anion:cation molar ratio highlighted the impact of the hydrophobic binding of excess surfactant monomers to the polycation-surfactant anion network on the phase transitions in the surfactant ion mixing plane phase diagrams for cat-HECDS.

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Abbreviations: cat-HEC, cationic hydroxyethyl cellulose; NaDS, sodium dodecyl sulfate; cat-HECDS, cationic hydroxyethyl cellulose dodecyl sulfate; cat-HECCL, cationic hydroxyethyl cellulose; SAXS, small-angle X-ray scattering; S:N, sulfur to nitrogen molar ratio; N_{agg} , aggregation number.

* Corresponding author at: James L. Winkle College of Pharmacy, University of Cincinnati Academic Health Center, 3225 Eden Avenue, Cincinnati, OH 45267-0514, USA.
 E-mail address: baalbanh@mail.uc.edu (N.H. Baalbaki).

1. Introduction

Polymers and surfactants are frequently used together, both unintentionally and intentionally, in cosmetic, industrial and pharmaceutical applications [1,2]. One such intentional use is surface conditioning of the skin and hair; here, cationic polymers are combined with cleansing anionic surfactants to mitigate harshness, boost conditioning and improve the deposition of feel enhancers and active agents [1]. In these applications, the cationic polyelectrolyte and surfactant anion electrostatically associate upon dilution through an ion-exchange process [2]. These insoluble complex salts can then bind to the keratin substrates and impart their conditioning benefits through mechanisms detailed by Goddard and Ananthapadmanabhan [1].

The properties and utility of these viscoelastic gel-like aggregates are influenced by their composition, specifically the charge density, charge location, backbone flexibility and molecular weight of the cationic polymer and the surfactant headgroup and chain length. Ultimately, the conformation of the polycation-surfactant ion complex is a balance of the preferred configuration of the polymer and most desirable packing arrangement of the surfactant [2]. Typical investigations into the structures of the dilute and concentrated phases produced after phase separation use characterization techniques to examine aqueous systems with cationic polymer and anionic surfactant at varying proportions. Li et al. identify these techniques and provide their own experimental data on the phase behavior and molecular thermodynamics of aqueous solutions of a cationic hydroxyethyl cellulose (cat-HEC) polymer, specifically Polymer JR 400, and sodium dodecyl sulfate (NaDS) [3]. This system provides favorable conditioning and deposition behavior and is in common commercial use [3,4].

Of particular interest to the controlled release of actives from these matrices are the phases and structures of the aggregates remaining on skin and hair after rinsing. This enduring delivery vehicle is the concentrated phase, likely with an excess of surfactant and equilibrated to a degree of partial hydration on the scalp. Svensson et al. simplified the study of the Polymer JR 400/NaDS concentrated phase by limiting their examination to the surfactant ion mixing plane of the complex salt, cationic hydroxyethyl cellulose dodecyl sulfate (cat-HECDS) [5]. Unlike the typically analyzed polymer-surfactant aqueous mixtures, here the complex salt with a 1:1 stoichiometric ratio of anions to cations was formed from Polymer JR 400 and NaDS, then washed of excess surfactant, isolated and dried. A ternary phase diagram for the lyophilized complex salt, water and NaDS was then constructed. This mixing plane explores the phases that occur in compositions with surfactant levels beyond saturation, where the coacervate network loosens and re-dissolves with excess surfactant (Fig. 1) [4,5]. This permits an *in vitro* examination of the system that is more similar to delivery matrix which remains on the skin.

The focus of this study was to apply this approach for mapping the phases and structures of polyion-surfactant ion aggregates to explore the impact of polyelectrolyte properties on the phase behavior of coacervate delivery vehicles. Specifically, the influence of charge density was chosen since electrostatic forces are a known modulator of the interaction between the polyelectrolyte and surfactant [6–8]. To explore the impact of charge density reduction on the phase behavior of cat-HECDS in the surfactant ion mixing plane, the complex salt method detailed by Svensson et al. was repeated for this study using the same molecular weight cat-HEC polymer with half the degree of charge substitution [5].

2. Materials and methods

2.1. Materials

Sodium dodecyl sulfate, NaDS, (purity >99%) was purchased from Sigma–Aldrich (St. Louis, MO) and used without additional purification. The chloride salt of cationic hydroxyethyl cellulose (cat-HECCL), designated commercially as UCARE™ Polymer or Polyquaternium-10, was obtained from the Amerchol Corporation (Philadelphia, PA), an affiliate of the Dow Chemical Company. Specifically, Polymer LR 400 was selected for its medium molecular weight and degree of cationic charge substitution. The molecular weight of the polymer is ~400,000 g/mol and degree of charge substitution is in the range of 0.17–0.24, calculated from the weight percent nitrogen (0.8–1.1%) provided by the supplier [9]. Milipore® filtered water was used in the synthesis of the complex salt and in the generated phase diagram compositions.

2.2. Making the complex salt

To produce the complex salt, a concentrated, homogeneous mixture of cat-HECCL and NaDS is prepared and then diluted below the critical micellar concentration of the surfactant resulting in the phase separation of the electrostatically associated complex salt, cat-HECDS. Svensson et al. details a procedure for making cat-HECDS with Polymer JR 400, similar in molecular weight but with twice the degree of charge substitution of LR 400 [5,9]. The method was applied here with adjustments made for the reduced degree of charge substitution and desired yield; an elemental analysis performed on Polymer LR 400 confirmed 0.84% nitrogen, equal to a 0.18 degree of substitution.

The complex salt was prepared in a 5-gallon plastic bucket with an overhead stirrer used for mixing. The concentrated mixture was made by slowly adding 1.12 L of a 2 wt% solution of cat-HECCL to 1.68 L of a 22 mM NaDS solution while stirring. To ensure a homogeneous mixture, the cat-HECCL solution was prepared as a slurry immediately prior its addition. This mixture was initially cloudy but cleared and began to thicken after approximately 3 h. Then, the concentrated solution was slowly diluted with 15 L of water while continuing to stir. A precipitate was noticed after the addition of as little as 5 L of water. The dispersion was mixed for another 3 h then allowed to sediment and agglomerate overnight.

The precipitate formed a gel-like cake at the base of the bucket and was washed until evidence of excess surfactant was no longer apparent. For the initial washing step, the bulk solution was decanted from and replaced with ~12 L of fresh water and the dispersion mixed and allowed to sediment. The next day, the solution was decanted again and the precipitate collected in smaller (50 mL) plastic tubes. These were centrifuged briefly (3–5 min at 1258 RCF) and the supernatant decanted. The precipitate was washed, centrifuged and decanted in these tubes until no foam was present during the washing step. After removing the supernatant a final time, the precipitate was collected and lyophilized. The water content of the complex salt before freeze drying was 93%. The water content in the dry complex salt was $11.4 \pm 1.5\%$ ($n=4$), measured gravimetrically by heat drying. The yield of the procedure was ~68%. An elemental analysis for nitrogen and sulfur was performed by an independent laboratory; the results showed a 1:1 stoichiometric complex was successfully formed.

2.3. Sample preparation

To map the regions of the surfactant ion mixing plane phase diagram, 60 compositions with variable wt% ratio of complex salt to water to NaDS were prepared for phase evaluation. Fig. 2 identifies the locations on the phase diagram corresponding to the compo-

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