Deposition from Conditioning Shampoo: Optimizing Coacervate Formation

Robert Y. Lochhead, Lisa R. Huisinga and Tara Waller

The Institute for Formulation Science,
The University of Southern Mississippi, Hattiesburg, Miss., USA

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ABSTRACT: *New techniques are being offered to produce formulations faster and more cost effectively than ever before. Researchers at the Institute for Formulation Science have addressed this challenge by developing robotic combinatorial techniques for the preparation and investigation of complex mixtures.*

Most conditioning shampoos depend on deposition of a polymer-surfactant coacervate to confer good wet-combing and manageability. Complex coacervate formation is crucially dependent on the molecular characteristics of the polymer and surfactant species, and it is significantly affected by the presence of other ingredients such as cosurfactants and dissolved salts. The optimization of these systems presents a challenge to the formulator because of the astronomical number of possible compositions with different performance outcomes.

Conventional formulation practice requires literally years of laboratory experimentation to characterize and optimize products that depend on complex coacervate formation. Robotic combinatorial techniques that accelerate the characterization and optimization of complex coacervate formulations have been explored at the Institute for Formulation Science. There has been success in constructing compositional phase diagrams that "fingerprint" the compositional range of complex coacervate formation as a function of polymer and surfactant molecular characteristics and the presence of other ingredients. These diagrams quickly guide the formulator to compositions of interest, and dramatically reduce the time and effort required for the screening of new ingredients, the formulation of new products and optimization of existing products. This article briefly describes the application of combinatorial techniques to the detailed study of complex coacervation from the system: guar hydroxypropyltrimonium chloride (and) sodium lauryl ether sulfate (and) water (*aqua*) (GHCSL)[a].

Conventional formulation practice requires literally years of laboratory experimentation to characterize and optimize products that depend on complex coacervate formation.

Goddard's original research into the nature of the interaction of cationic polymers with anionic surfactants formed the technological platform for modern conditioning shampoos.[1] For systems comprised of a cationic hydroxyethylcellulose and anionic surfactants, Goddard showed that below the surfactant critical micelle concentration (CMC), an insoluble coacervate phase was formed and this phase was resolubilized at a surfactant concentration that was above the CMC. This mechanism formed the basis of the now familiar dilution-deposition concept for conditioning shampoos that relied on formulation of the solubilized coacervate in the shampoo and deposition of phase-separated coacervate as the system was diluted below the CMC upon rinsing.

However, behind this apparently simple mechanism there lies a complexity that continues to engage formulators to this day. Thus, patents continue to be issued in this area although more than 30 years have passed since the original discovery. The nature of the coacervate in these systems critically depends on factors such as polymer molecular weight, charge density, charge density distribution, and details of surfactant structure, cosurfactant ratio and the presence of electrolyte.

The coacervate properties must depend upon the conformation of the cationic polyelectrolyte and the hydration of that polyelectrolyte. The conformation of the polyelectrolyte depends, in turn, upon the ionic strength of the system as well as the exact nature of the ion-exchange process that causes surfactant to bind to the cationic sites.

The overall hydration will be affected by the availability of water binding groups such as hydroxyl groups on the polymer. Interaction of the cationic polymer with anionic surfactant micelles would be expected to change the micellar structure. It is well known that an increase in ionic strength will cause structural transitions from spherical to

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[a] *INCI: name Guar hydroxypropyltrimonium chloride (and) sodium laureth sulfate and water (aqua)*

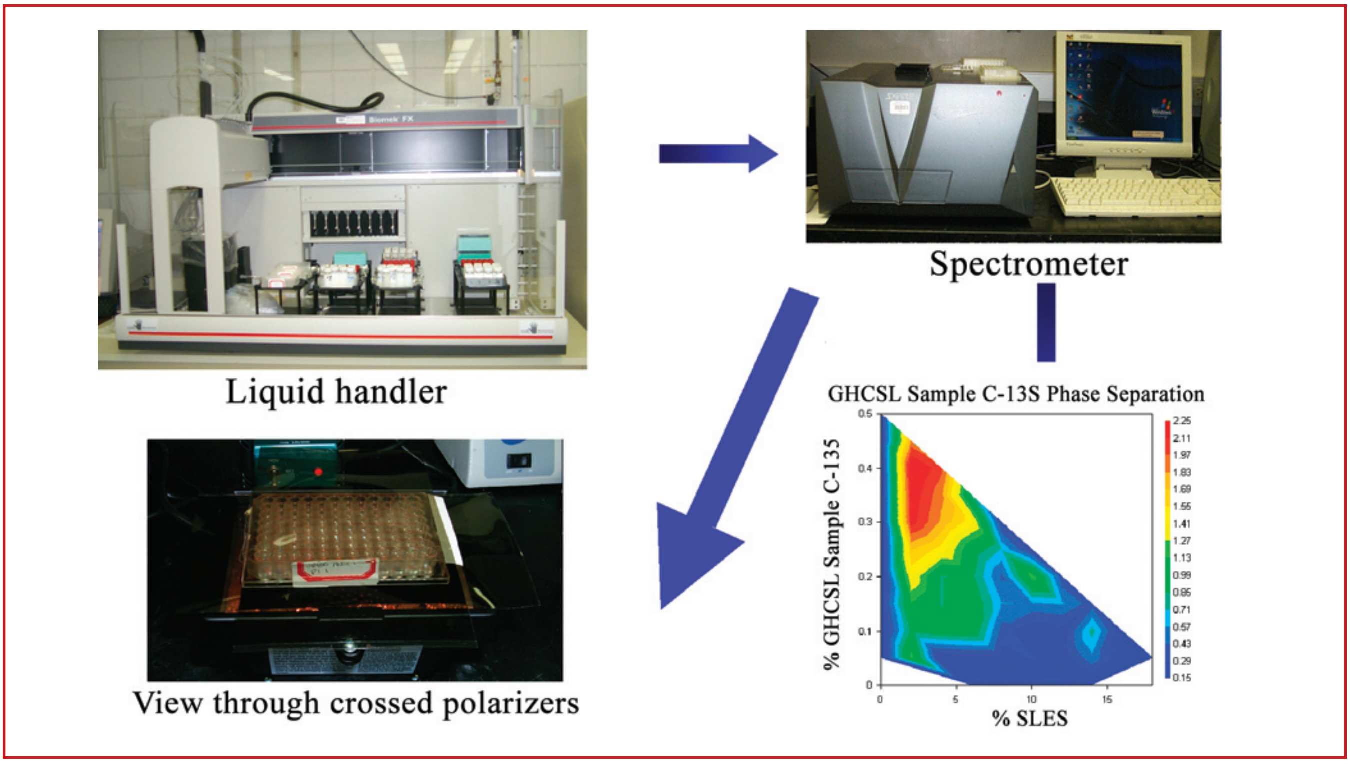

Figure 1: A combinatorial approach to the formulation of liquid products

rod-like micelles, worm-like micelles or even lamellar phase. All of these micellar structures have distinct rheological properties and kinetics. Prediction and optimization of these systems is complicated by the complexities of the interactions. Alternatively, empirical formulation for ultimate understanding and optimization of the systems would require the study of a large number of possible polymers, charge densities, structures, molecular weights, surfactant types and ratios, ionic strength and electrolyte type. Such a study would require an army of formulators or a very long time to complete.

This challenge has been addressed by the Institute for Formulation Science with its development of robotic combinatorial methods for the study of these types of formulation problems requiring the generation of large data sets. At the present time researchers at the institute are engaged in developing their understanding of complex coacervates systems by the rapid generation and investigation of thousands of formulations in short time periods. The properties of these formulations are plotted as composition diagrams to guide the formulator.

The Combinatorial Investigation of Complex Coacervation

At the current time, the preferred method for the preparation of complex mixtures at the institute is to utilize a robotic liquid handler[b] and

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[b] *A product of Beckman-Coulter, Inc., Fullerton, Calif., USA*

to prepare mixtures in 96-well plates in which each well contains a sealable glass vial of appropriate size for the system being studied. The robotic equipment is limited to handling low-viscosity liquids. Therefore, researchers at the institute have developed multiple manual pipetting techniques to handle high-viscosity liquids.

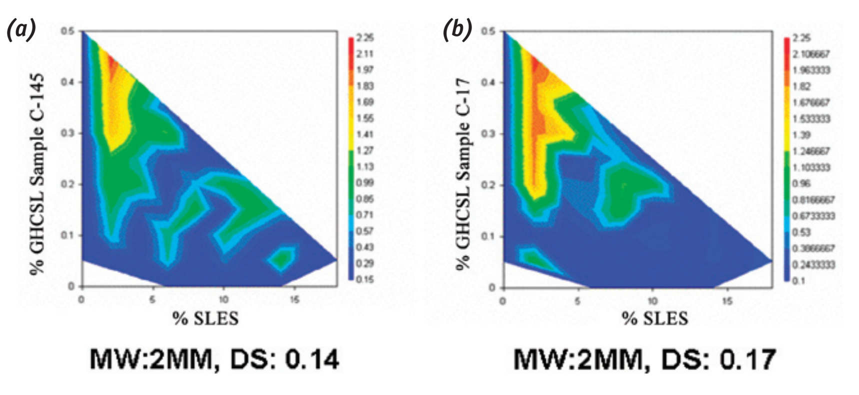

Figure 2: Composition diagrams for GHCSL. The diagrams are color-coded in accordance with the visual spectrum with blue representing the absence of coacervate and red indicating the maximum concentration of phase-separated coacervate. Each diagram was constructed from observations on at least 368 separate compositions and each composition was duplicated to check accuracy. The molecular weight was identical for both cationic guars but the degree of cationic substitution is 0.14 in diagram (a) and 0.17 in diagram (b).

New pipette tips were used for each solution in order to avoid cross-contamination of the samples. When high throughput screening is conducted, it is necessary to include standard compositions to ensure the accuracy of the results; because instruments do drift with time, components such as pumps can fail. It is important to correct these deviations to avoid flawed data. With this in mind, at least two standard compositions in each 96–well plate were included and the measured values of these compositions were plotted. Any significant deviation was investigated immediately and, if necessary, corrective measures were taken.

The compositions were mixed by vortexing the 96-well plate. In order to ensure that the samples adequately were mixed, two dyed samples were included in each 96-well plate. Measurement of λ_{max} of the dye solution was a monitor for adequate mixing (see Figure 1).

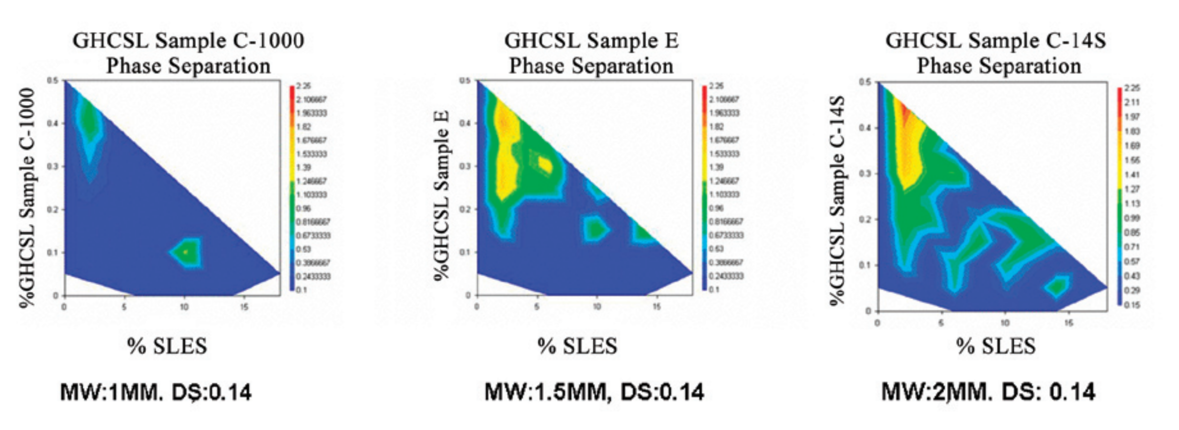

Figure 3: Composition diagrams showing regions of coacervate formation for GHCSL for cationic guars having the same change density but different molecular weights.

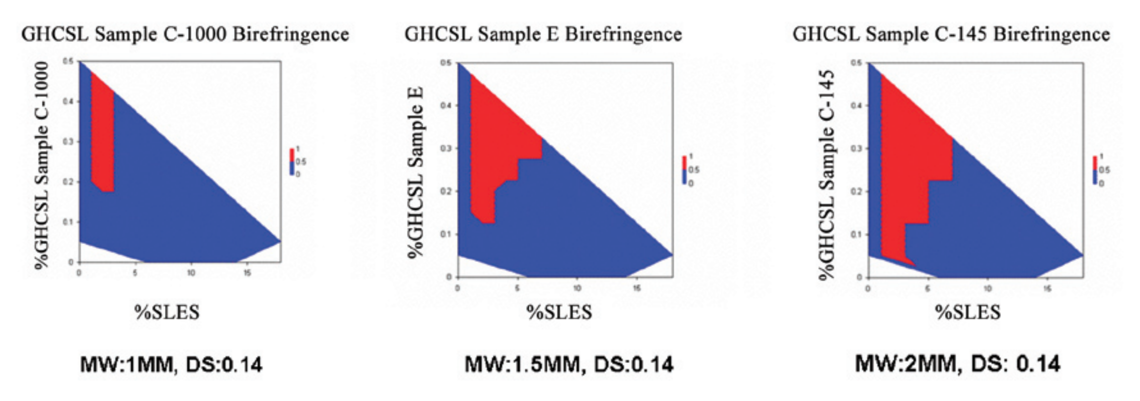

Figure 4: Composition diagrams showing regions of birefringent compositions for GHCSL for cationic guars having the same change density but different molecular weights. Birefringent compositions are shown in red.

High Throughput Analytical Techniques

Measurement using light or other common electromagnetic radiation is quick and nondestructive. Therefore, whenever possible, a spectrometer[c] capable of reading 96 samples as a single batch was utilized. This instrument provided the capability to measure entire spectra, to measure wavelength shifts and to measure concentrations of desired species in a few minutes using Beers' Law.

The samples were viewed through crossed polarizers to detect birefringent phases such as liquid crystals. Microviscosities were measured by observing depolarization of biphenyls. The amount of coacervate in a sample was assessed by measurement of the absorbance in the visible region.

The data was collected in an interactive database and then visualized as color-coded composition maps. These composition maps showed the volume of complex coacervate formed as a function of polymer structure and composition, surfactant composition and electrolyte concentration. In original work to date, these maps have been shown to be distinctive for each polymer investigated. The precise mechanisms of coacervate formation and the driving forces involved were deduced from the characteristic patterns in the maps.

An important and usually time-consuming aspect of each of the studies is the validation of the high throughput experimentation methods with standard laboratory procedures and confidence that the methods will scale-up reliably.

Results

Cationic polymers, such as guar hydroxypropyltrimonium chloride, provide hair conditioning from shampoos. Guar hydroxypropyltrimonium chloride compounds, with varying molecular weights and charge densities, were combined with the anionic surfactant sodium lauryl ether (3EO) sulfate to form complex coacervates. Generating more than 350 compositions for each polymer/surfactant combination, researchers used high-throughput screening formulation methods to identify the structure and amount of coacervate formed. These results were represented using contour phase diagrams in order to map specific areas to study in detail. The detailed structures of the lyotropic association colloids that were selected from Figures 2, 3 and 4, were identified using polarized light microscopy.

There is a minimum polymer concentration that must be exceeded for coacervate formation to be observed.

One might expect that coacervate amount and composition range would increase with increase in polymer charge density. This indeed was ob-

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[c] *The Safire UV/VIS is a product of Tecan Systems, Inc., San Jose, Calif., USA.*

served as displayed in Figure 2, which shows increased amounts of coacervate as the polymer cationic charge density is increased from 0.14 to 0.17 moles per equivalent anhydroglucose unit.

The influence of polymer molecular weight on coacervate formation can be seen from Figure 3. Each of the three cationic guar samples possessed the same degree of cationic substitution (0.14), but they ranged in molecular weight from 1 million daltons (d) to 2 million d. It clearly is observed that the amount of coacervate formed increased in amount and concentration range as the polymer molecular weight was increased, despite the constancy of polymer charge density. There is a minimum polymer concentration that must be exceeded for coacervate formation to be observed. The lowest molecular weight polymer displays two islands of coacervate formation. It is suspected that this indicates two distinct mechanisms; one relying primarily on ion-exchange between the polymer and the anionic surfactant, and the other being driven by a change in surfactant micelle size and shape.

It is reasonable to assume that the interaction between oppositely charged polymer and surfactant should result in a collapse of the electrical double layers of both species. If this is the case, the response of the surfactant micelle should be to increase in size and to adopt a shape having lower surface curvature. Ultimately, the micelles might be expected to grow into lyotropic liquid crystals. Anisotropic lyotropic liquid crystals are optically birefringent; that is they rotate the plane of plane-polarized light. If lyotropic liquid crystals are present, they should be detectable by observing the compositions through crossed polarizers. This experiment was conducted for the systems shown in Figure 3. The result of the birefringence measurements are shown in Figure 4.

It is notable that the compositional regions of birefringence correspond closely to the coacervate compositions reported in Figure 3. It was concluded, therefore, that the micellar structure of these coacervates is lyotropic liquid crystalline in nature.

Summary

Today's competitive environment demands that formulators produce tangible results at a greatly accelerated pace. Composition maps can be constructed rapidly to clearly show the effect of polymer molecular weight and charge density on the composition range of coacervation. Studies of birefringence indicate that the coacervates contain lyotropic liquid crystals. The composition maps provide valuable direction to formulators and can accelerate the development of new products and novel intellectual property.

References

Send e-mail to Robert Lochhead at robert.lochhead@usm.edu

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