# A study of the distribution of polymer/surfactant coacervate between solution and foam in archetypal shampoo systems

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**Synopsis**

The research reported here attempted to answer the question, "is the foam important in delivering coacervates from shampoos." In order to answer this question, we have measured the amount of polymer in the foam and in the liquid phases of several cationic polymer/anionic surfactant systems by gravimetry and by FTIR techniques. In all cases studied, we discovered that the concentration of solids and, especially the polymer, in the liquid phase and in the foam phase were essentially the same. We conclude that the foam is unlikely to be an important factor in the topical delivery of polymer/surfactant coacervates.

## INTRODUCTION

Two-in-one shampoos commonly depend upon triggered complex coacervation to deposit materials on the hair. The general mechanism that underpins these stimuli-responsive systems is known: the coacervate is solubilized at shampoo concentrations but separates as a liquid phase when the shampoo composition is diluted during rinsing. The coacervate deposits on the hair to confer conditioning benefits and it can also act as a delivery system for the deposition of other components such as silicones or anti-dandruff ingredients.

To date much of the study of coacervate deposition on hair has been focused on liquid systems. However, in the real application, the shampoo is foamed on hair prior to rinsing. This raises the question of the significance of the surfactant foam on the delivery of coacervate to the hair surface. This is a reasonable question because, in processes such as mineral froth flotation, hydrophobic particles are readily separated from hydrophilic particles and concentrated in the froth.

In shampoos, lather is believed to give the consumer a perception of cleansing as they use the product. To achieve this rich lather, companies include surfactant concentrations greater than those needed to cleanse even the most soiled hair (1). In 2-in-1 shampoos, cationic polymers form complex coacervates that separate upon dilution and deposit on the hair and scalp surfaces to deliver components that confer attributes such as ease of combing and anti-dandruff properties. The question that we were trying to answer in this

research was, "how important is the shampoo foam on the eventual deposition of the co-acervate?" The first stage of this investigation, reported here, was to determine if coacervate was concentrated in the foam.

CONDITIONING SHAMPOOS

Conditioning is a term used in hair shampooing. Conventional Conditioners are usually based on cationic surfactants and alkanol co-surfactants. In the present case, however, conditioning is achieved by the triggered deposition of complex coacervates comprising cationic polymer and anionic surfactant. The conditioning polymer is used at relatively low levels; usually less than 1% by weight is incorporated into the shampoo, which contains from about 10 to 20% anionic surfactant(s). Upon dilution with water, complex coacervate (formed from the cationic polymer and anionic surfactant) separates from solution as the shampoo is rinsed from the hair (2).

The quaternary polymers investigated in this study were Polyquaternium-7, Polyquaternium-10, Polyquaternium 76, and Polyquaternium-88, the chemical formulae of which
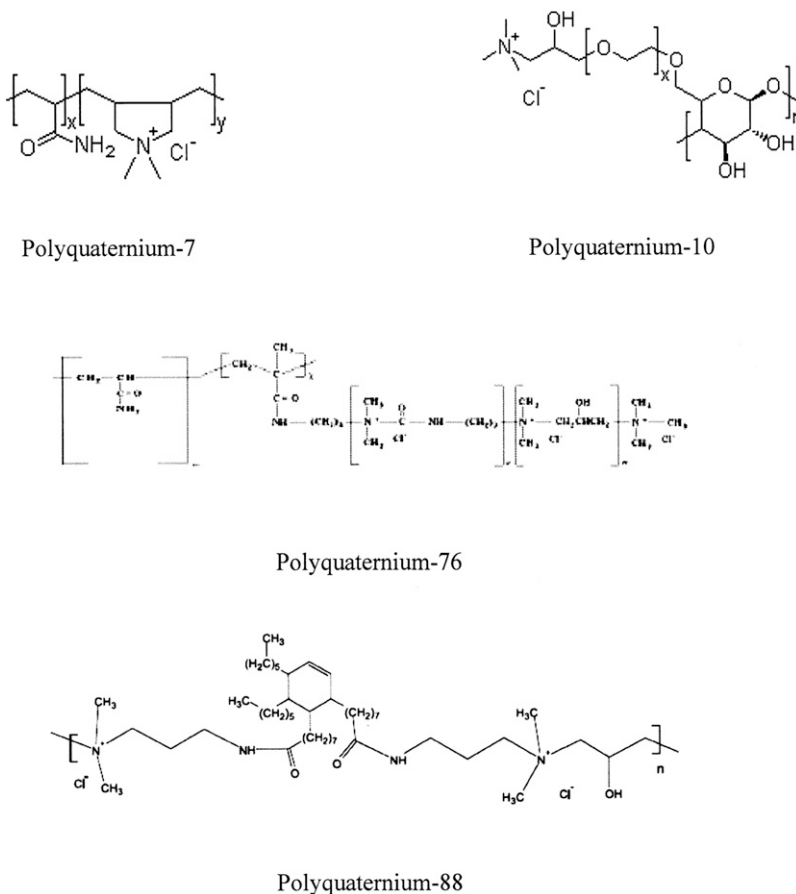


Polyquaternium-7

Polyquaternium-10

Polyquaternium-76

Polyquaternium-88

**Figure 1.** Structures of cationic polymers used in this study.

are shown in Figure 1 above. Polyquaternium-7 and -10 were used because of their known coacervate formation and use in personal care products. Polyquaternium-76 and -88 are two relatively new polymers that are slated for this application.

Two of the most common surfactants used in body care in combination with the cationic polymers are sodium lauryl sulfate (SLS) and sodium laureth sulfate (SLES) (Figure 2).

Sodium laureth sulfate is commercially available in a range of degrees of ethoxylation. The most commonly used variants have degrees of ethoxylation ranging from one to three. Many co-surfactants have also been used in commercial shampoos, principally cocobetaines and distearates. However, this study was directed only to the interaction with the primary anionic surfactants. Our experiments were limited to SLES with two ethylene oxide groups. This molecule is abbreviated as SLE2S or SLES-2EO.

POLYMER/SURFACTANT INTERACTIONS

The aggregation process of coacervate formation between oppositely charged polyelectrolytes and surfactants with has been explained by Dubin and coworkers (3) as electrostatic interactions between the oppositely charged polymer molecules and surfactant micelles in which there are two distinct regions of coacervate formation at different micelle charge densities. The Dubin model indicates that micelle charge density controls coacervate formation. For oppositely charged polyelectrolyte and surfactant molecules, the surfactant binds to the polyelectrolyte due to electrostatic attractive forces. As the complex neutralizes, coacervation occurs as the intrapolymer complexes develop into interpolymer aggregates. At higher micelle charge density, coacervate precipitation occurs due to strong electrostatic interactions. Polyquaternium-7 and Polyquaternium-10, have been used in formulations over the last 30 years. They have large differences in charge density[4]. According to the Dubin model, these differences of charge densities explain the different interactions these polymers have with surfactants in a system.

On the other hand, Goddard *et al.* (5–7) have proposed that the coacervate formation process is a site-specific ion-ion interaction. Here, the cooperative process between the electrostatic interaction and hydrophobic association/segregation governs complex formation. The association between the surfactant anion and the polymer cations is driven by the resultant loss of free energy. Thus, a loss of enthalpy accrues from the ionic attraction between polyions and surfactant ions of opposite charge, and the release of soluble counter-ions into the surrounding media results in a gain in configurational entropy. The formation process is also driven by hydrophobic interaction between tail groups of the bound surfactant molecules, resulting in intramolecular and intermolecular association of these groups.

Goddard *et al.* (5,7) and other researchers (8,9) observed that complexes formed between the oppositely charged polyelectrolyte and surfactant system depends on the surfactant concentration and involves surfactant binding, phase separation and resolubilization.



**Figure 2.** Structures of sodium lauryl sulfate and sodium laureth sulfate.

Goddard (7) and other researchers (10,11) demonstrated that above the critical concentration of the surfactant, known as the critical aggregation concentration (CAC), of the surfactant site-specific interactions occur between anionic surfactant molecules and cationic sites along the polymer backbone. Increased interactions between the polymer and surfactant molecules are driven by increasing the surfactant concentration. However, a threshold occurs where the polymer-surfactant complex phase separates from the aqueous solution to form a polymer-surfactant coacervate. As the concentration of the surfactant is increased above the critical micelle concentration (CMC) of the polymer-surfactant system, the coacervate can become soluble to form a single phase system.

The basic, yet unresolved, difference between Goddard's hypothesis and Dubin's hypothesis derives from Goddard's explanation that coacervation results from single ion-ion interaction whereas Dubin's explains the phenomenon as arising from a colloidal interaction between the polyelectrolyte and the surfactant micelles.

COACERVATE IN THE FOAM

Upon foam formation (Figure 3), surfactant molecules adsorb at the air–water interface of the foam film.

As discussed above, at certain concentrations of polymer and surfactant, coacervates form in the solution. As foaming/lather formation occurs, it has been explained that the coacervate present in the solution is adsorbed into the crust of the foam lamella as shown in Figure 4. The high viscosity coacervate gel is present in the lamella crust, while the low viscosity phase is present in the lamellar core (12).
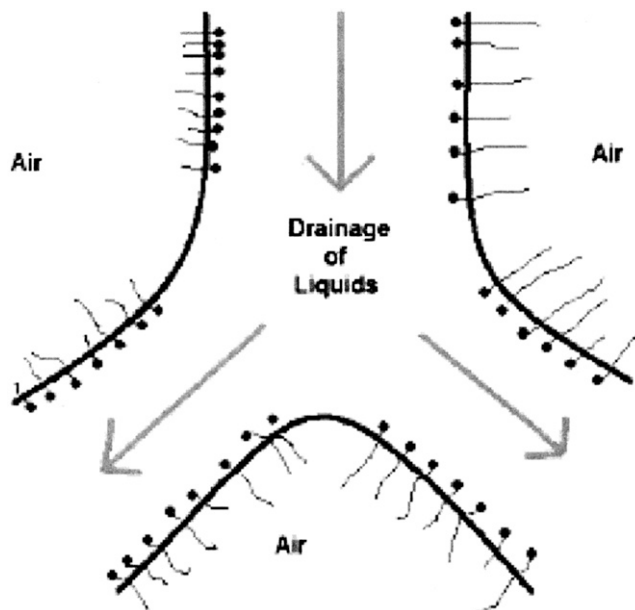


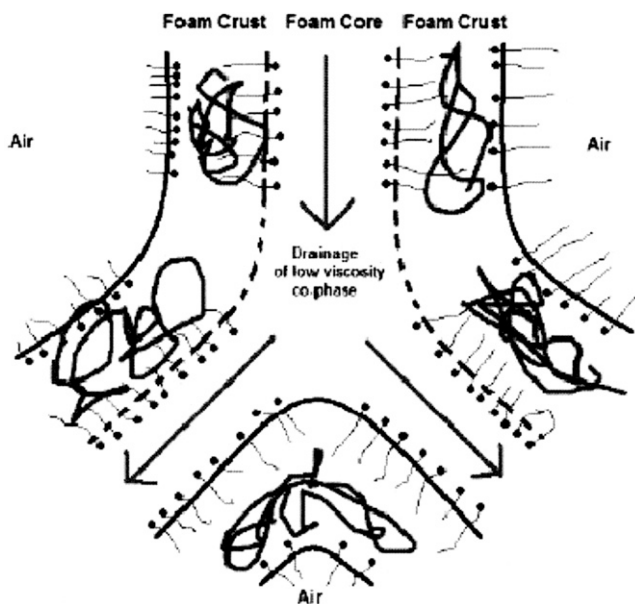**Figure 3.** Schematic of surfactant alignment during foam formation.

**Figure** 4.  Schematic of coacervate presence in foam.

RESEARCH GOALS

The goal of this project was to investigate the distribution of separated complex coacervate between the solution and foam phases. The experimental plan set out to determine (1) what is in the foam phase? (2) How much of it is polymer, surfactant or coacervate? (3) Does this change with concentration? (4) Does the change in concentration correspond to the phase diagram? The overall goal was to determine where the coacervate is present in the solution, foam or liquid.

**EXPERIMENTAL**

MATERIALS

Polyquaternium-7 used was Merquat® S supplied as a 9%wt liquid by Nalco Company. UCare® Polymer JR-30M (Polyquaternium-10) from Dow Chemical Company was used as supplied. Mirapol® AT-1 (Polyquaternium-76), supplied from Rhodia Canada Inc., was used as a 10% wt solution, and Cola® Quat PDQ (Polyquaternium-88) was supplied by Colonial Chemical, as a 35.8% solution in water. The surfactant used was Standapol® ES-2 (SLE2S) supplied by Cognis Corporation as 35.8% wt solution in water. Deionized water (DI water) was used as the only solvent throughout this research. All materials were used as received.

POLYMER SOLUTIONS AND SURFACTANT SOLUTIONS

The weight percent of polymer and surfactant in each of the provided solution was furnished by their respective suppliers. The solutions of these polymers and surfactant were

used as is, except for the Polyquaternium-10, which was provided as a solid. In this case a 1% solution was prepared in DI water prior to experimentation.

Polymer solutions were prepared of 2% Polyquaternium-7, 0.5% Polyquaternium-10, 2% Polyquaternium-76, and 2% Polyquaternium-88. A 15% solution of SLE2S was also prepared. Using a combinatorial liquid handler, 136 different combinations of polymer and surfactant concentrations were prepared in microwells, using only one polymer at a time. The absorbance of each sample was determined using a Tecan UV-Vis spectrophotometer at the maximum absorbance wavelength, which occurred at 600 nm for each of the plates. 10 scans were obtained at different locations within each well to detect the presence and to estimate the approximate amount of coacervate present.

Solutions of 0.5% polymer and 15% SLE2S were prepared using polymers, Polyquaternium-7, Polyquaternium-10, Polyquaternium-76, and Polyquaternium-88. These solutions were used as the stock solutions throughout this project. Each of the stock solutions was diluted using a stock solution to water ratio of 9:1, 4:1, 7:3, 3:2, 1:1, 2:3, 3:7, 1:4, and 1:9. The dilution path was plotted on each phases diagram.

A Nikon Optiphot2-Pol polarizing microscope with a Kodak DSC 290 Zoom Digital Camera attachment was used to capture images of the foam prepared upon shaking the Polymer/surfactant dilutions. Samples were prepared by shaking the scintillation vials containing each of the dilutions using a Vortex Genie 2 Shaker for three minutes to form a foam layer. The foam and liquid phases were each placed in an oven at 80°C for 4 hours. The percent solids was determined from the dry weight for each sample.

POWDER FT-IR SPECTROSCOPY

A Nicolet 6700 FT-IR with a diamond ATR probe was used with a resolution of 2 cm$^{-1}$ at 32 scans per sample. Spectra were determined for each of the dried foam and liquid phases, as well as dried samples of the polymer solutions and surfactant solution. OMNIC software was used to compile and compare the data.

## RESULTS AND DISCUSSION

PSEUDO–PHASE DIAGRAMS

Phase behaviors of the polymer/surfactant/water systems were plotted on composition maps as pseudo-phase diagrams, shown in Figure 5.

The dilution lines for each poymer are shown in the phase diagrams of Figure 5. It is important to note here, however, that there are limitations with this method when the coacervate is not homogeneously dispersed within the composition, or when it does not separate as a distinct layer. For each of these polymers, there were instances in which coacervate was observed visually to adhere to the side of the well. In these cases the
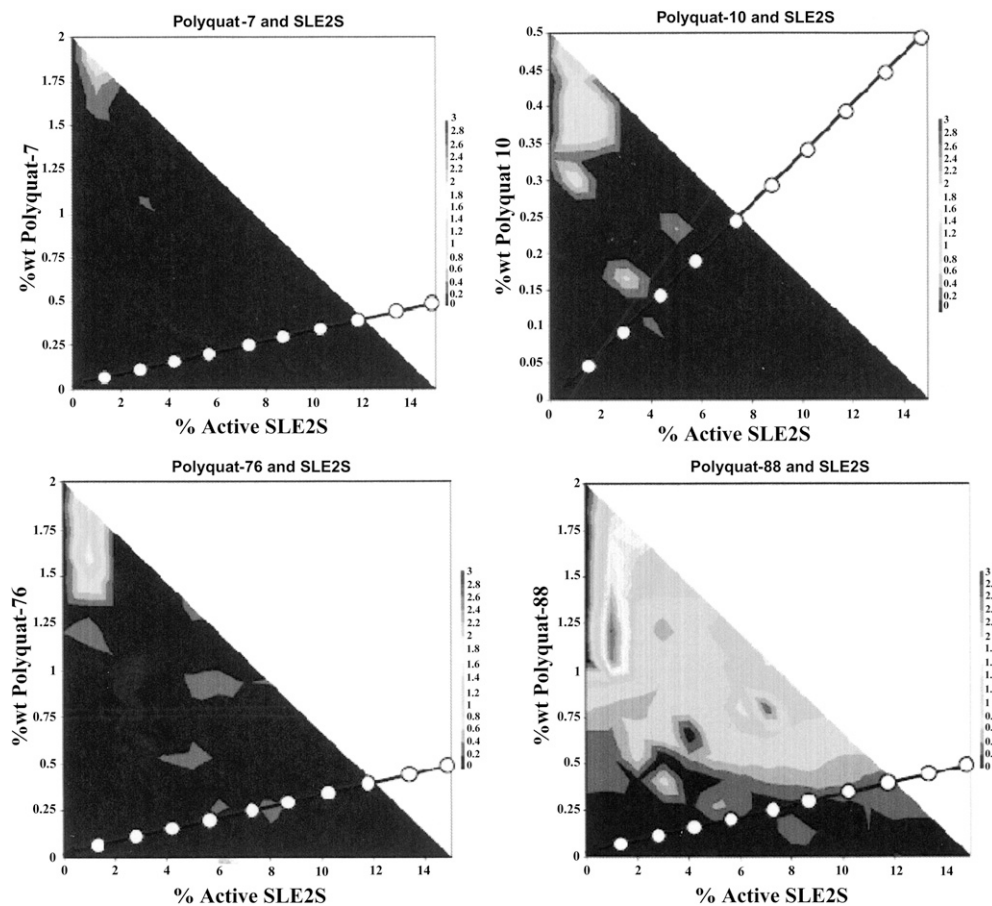
**Figure 5.** Contour phase diagrams. The lines represent dilution lines and the points represent the dilutions prepared.

coacervate could not be detected by the UV-Vis spectrometer. It was important, therefore, to visually observe each plate and to identify in which the coacervate was unobservable by the detector, and to eliminate these samples from our overall analysis.

The images of the serial dilutions are shown in Figure 6 are in order of decreasing concentration, as represented by the points in Figure 5. The opacity of the Polyquaternium-76 and Polyquaternium-88 are due to the relative insolubility of some polymer components within these samples, and not necessarily due to the presence of coacervate.

PERCENT SOLIDS IN FOAM AND LIQUID PHASE

Solids concentrations for the foam and liquid phases formed, for each of the polymer/surfactant solutions, were determined gravimetrically by drying the liquid and foam fractions and measuring the percent solids remaining. The percent solids in the foam and liquid appear to be statistically identical, decreasing linearly as the percent of the stock solutions decreases (Figure 7).
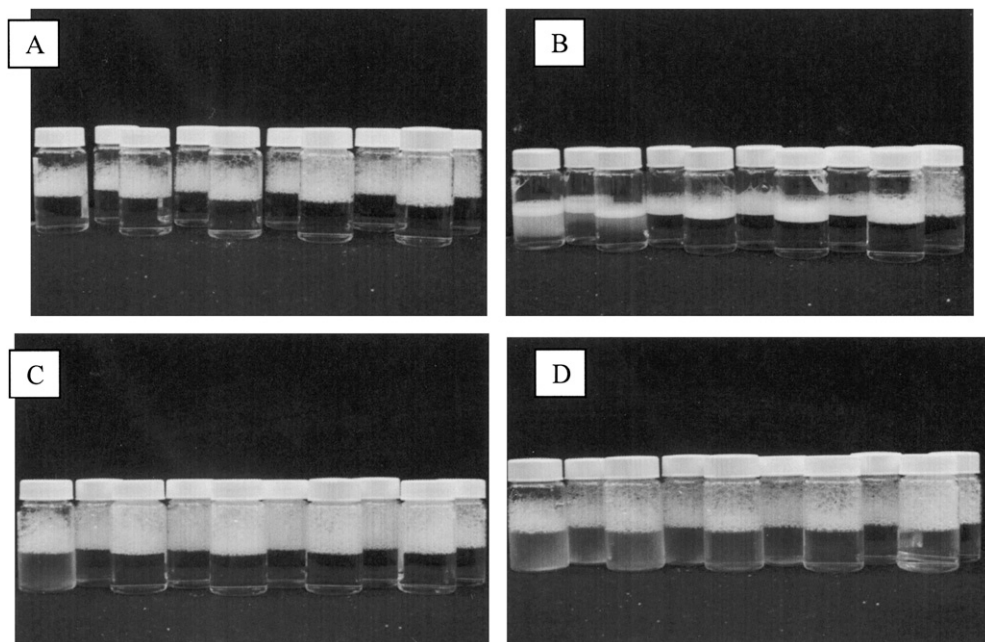
**Figure 6.** Photographs of solution with visible liquid and foam layers after shaking. (A) Polyquaternium-7. (B) Polyquaterium-10. (C) Polyquaternium-76. (D) Polyquaternium-88.

In all cases, the solids content of the foam and liquid phase were approximately equal. This indicates that there is not preferential concentration of the solids ingredients by the foam phase.

POWDER FT-IR ANALYSIS OF FOAM AND LIQUID PHASES

Fourier-Transform Infrared Analysis (Figure 8) was performed on the dried foam and liquid phases to determine the amounts of polymer in each of the phases.

The peak from 3700 to 3000 was determined to be the identifying peak for each of the polymers, because of its absence in the SLE2S trace. The N-H and O-H peaks are both represented in this region. For Polyquaternium-7, Polyquaternium-76, and Polyquaternium-88, these peaks represent N-H. For Polyquaternium-10, the peak in this region represents the O-H peaks of the polymer. Using the integral under this peak, the ratio of polymer in the foam to polymer liquid of the same dilutions was calculated and plotted, as shown in Figure 9.

The ratios of (polymer in the foam phase):(polymer in liquid phase) clustered around the value of 1. This experiment provided no evidence for selective fractionation of the polymers and their associated coacervates in either the foam of liquid phases.

CONCLUSIONS

Polymer/surfactant complexes are important for deposition of materials such as silicone via shampoo and body wash formulations. These complexes, commonly referred to as
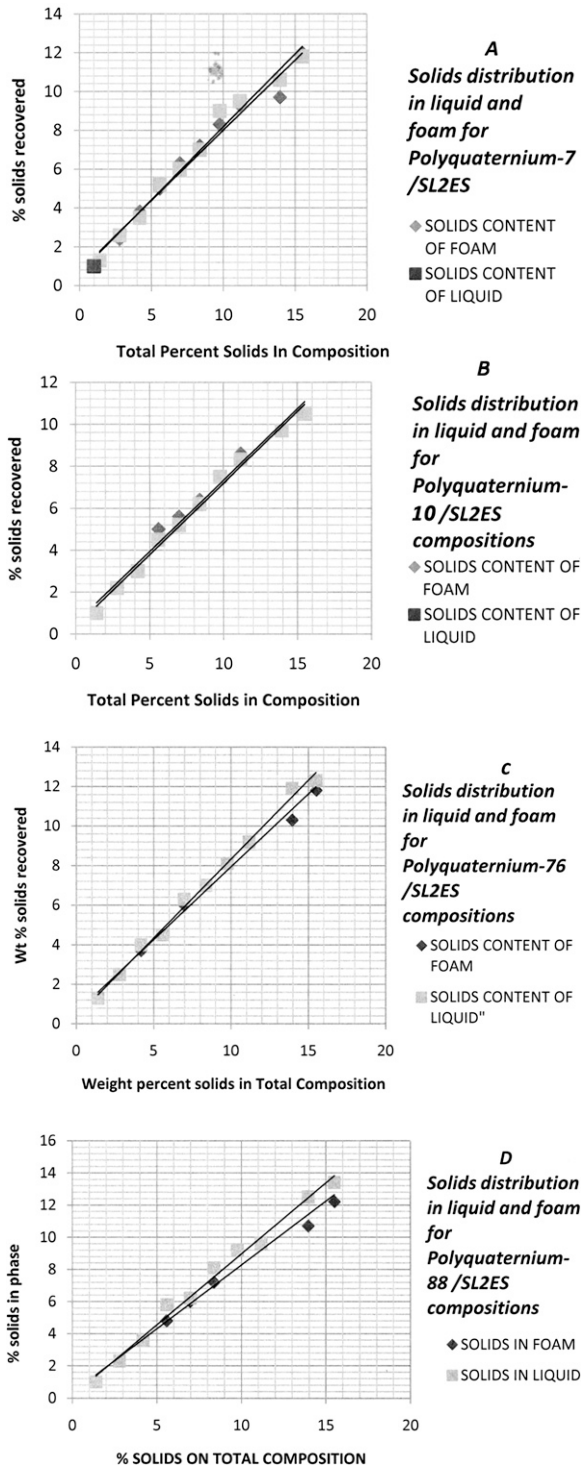
**Figure 7.** Percent solids in foam and liquid phases as a function of dilution in water for (A) Polyquatrnium-7, (B) Polyquaternium-10, (C) Polyquaternium-76, and (D) Polyquaternium-88.
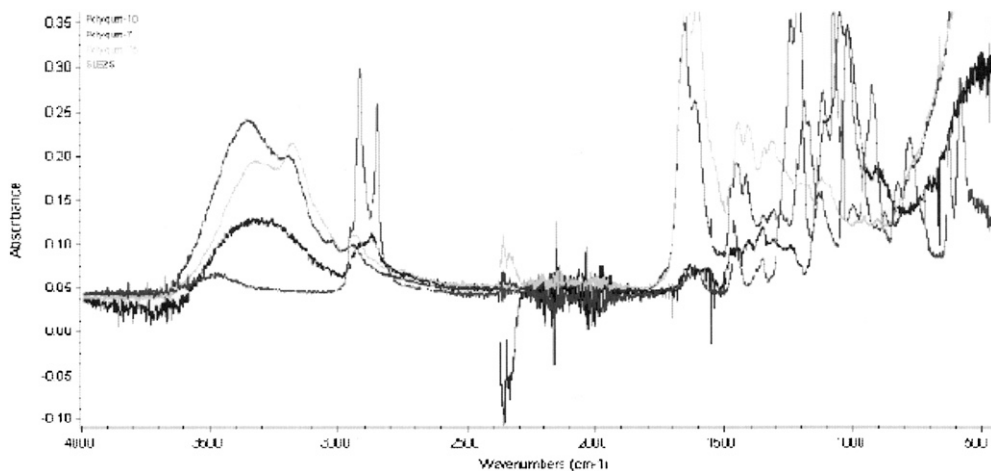
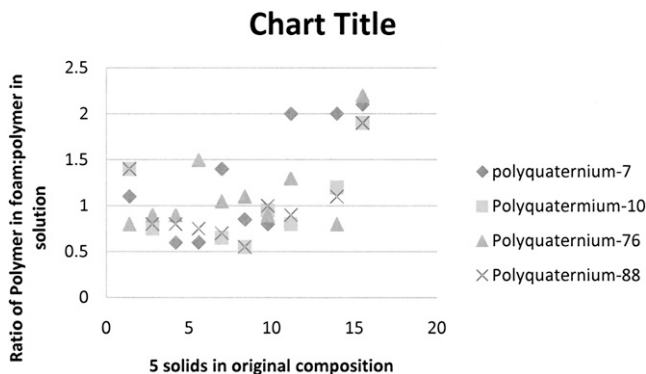**Figure 8.** FT-IR of polymers and surfactant.



**Figure 9.** FT-IR derived ratio of polymer in foam phase to liquid phase.

coacervates, form upon dilution of a concentrated polymer/surfactant solution, and deposit directly onto the hair and skin to provide conditioning effects as well as deposit other molecules to achieve lasting feel. These complexes are found in the foam and liquid phases. Our experiments, reported here, have shown that there is no preferential concentration of polymer in the foam phase compared to the liquid phase for all of the polymers studied. We conclude, therefore, that foam fractionation of the polymer/surfactant coacervate is unlikely to be an important factor in the topical delivery of these coacervates.

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