Use of statistical modeling to predict the effect of formulation composition on coacervation, silicone deposition, and conditioning sensory performance of cationic cassia polymers

CAROLE LEPILLEUR, JOHN MULLAY, CAROL KYER, PAM McCALISTER, and TED CLIFFORD, *Lubrizol*

Advanced Materials, Inc., Noveon® Consumer Specialties,

9911 Brecksville Road, Brecksville, OH 44141.

Synopsis

Formulation composition has a dramatic influence on coacervate formation in conditioning shampoo. The purpose of this study is to correlate the amount of coacervate formation of novel cationic cassia polymers to the corresponding conditioning profiles on European brown hair using silicone deposition, cationic polymer deposition and sensory evaluation. A design of experiments was conducted by varying the levels of three surfactants (sodium lauryl ether sulfate, sodium lauryl sulfate, and cocamidopropyl betaine) in formulations containing cationic cassia polymers of different cationic charge density (1.7 and 3.0m Eq/g). The results show formulation composition dramatically affects physical properties, coacervation, silicone deposition, cationic polymer deposition and hair sensory attributes. Particularly, three parameters are of importance in determining silicone deposition: polymer charge, surfactant (micelle) charge and total amount of surfactant (micelle aspect ratio). Both sensory panel testing and silicone deposition results can be predicted with a high confidence level using statistical models that incorporate these parameters.

INTRODUCTION

Common conditioning shampoos are formulated with cationic polymers such as cationic cellulose or cationic guar derivatives which are compatible in the shampoo formula, but become incompatible upon dilution with water. The literature suggests that upon shampoo application, foaming, washing and rinsing, such cationic polymers form a complex with anionic and amphoteric surfactants that phase separates from the bulk solution, at surfactant concentrations below their critical micelle concentration (cmc). This phase separation or coacervation is known also as the "Lochhead effect" (1). The phase separation upon dilution has been mainly explained in the literature through coulombic attraction between anionic function of the surfactant and the cationic groups of the polymer. Goddard *et al*. (2) described that, at low surfactant concentration (below the cmc), anionic surfactants condense on the polycations. The resulting ion pair converts the cationic sites into hydrophobe-substituted sites. These hydrophobic interactions within and between

the polycations cause a phase separation. The phase separation persists if the positive and negative charge equivalent ratio is at stoichiometry. Above the surfactant cmc, co-micellization of the cationic polymer with the surfactant results in a one-phase soluble complex or clear system. The coacervate is often described as a gel-like phase that contains a high level of cationic charge and is known to deposit the polymer on negatively charged hair, forming a clear film (3-5). In addition, the coacervate aids in the deposition of insoluble actives such as silicone. The coacervation behavior and the type of coacervate formed vary depending on many criteria such as the cationic polymer characteristics (charge density and molecular weight), the cationic polymer concentration, the surfactant package used in the formulation, the ionic strength, pH and temperature. Li *et al.* (6) reported that the type or rheology of the coacervate formed influences the conditioning response. For instance, a highly charged cationic cellulose polymer may form a solid, granular, gel-like coacervate with low water content over a narrow dilution range that tends to be substantive and provide body to hair. A polymer with lower charge density may form a liquid-like gel with high water content over a wide dilution range that may be associated with soft feel and volume enhancement for hair. The molecular weights of these cationic polymers were shown to influence the amounts of coacervate, where the high molecular weight polymers formed more coacervate than the low molecular weight polymers.

The objective of this study is to determine the effect of the surfactant formulation composition on the conditioning performance of novel polymers based on cassia galactomannans. A design of experiments, as illustrated in Figure 1, considers the influence of the levels of three surfactants commonly used in shampoos; sodium lauryl ether sulfate (SLES-3), sodium lauryl sulfate (SLS), and cocamidopropyl betaine (CAPB) in formulations containing different cationic cassia polymers. It is known that the formulation composition has a dramatic effect on physical properties (viscosity, clarity, turbidity) and also on the coacervation behavior (7,8). The purpose of this study is to try to correlate the amount of coacervate formation to the conditioning profiles on European brown hair through the deposition of a small particle size silicone emulsion (average silicone droplet size of about 0.5 μm).
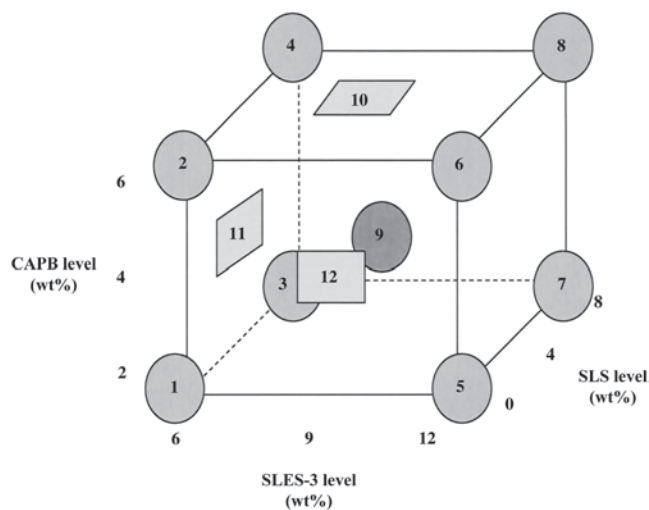

Figure 1. Design of experiments for shampoo formulations using surfactant combinations containing various levels of SLES-3 (x axis), CAPB (y axis) and SLS (z axis) (12 formulations).

EXPERIMENTAL

MATERIALS

Cassia gum is a natural vegetal carbohydrate based on mannose and galactose sugars extracted from the endosperm of the seed of cassia *tora* and cassia *obtusifolia*. It is a member of the galactomannan family of polysaccharides with a ratio of mannose to galactose content of at least 5:1. Cassia grows wild in tropical zones around the world. Cassia has been used for over a thousand years in Ayurvedic and Chinese medicine to treat skin ailments, indigestion, and pain. It is also used today as a gelling agent in pet and human food applications. The chemical structure of cassia gum is illustrated in Figure 2. Polysaccharide derivatives have a long history of use in personal care applications as thickeners, conditioning polymers, deposition aids and film formers. Cationic derivatives of guar gum, another galactomannan, have been successfully used in conditioning shampoos in combination with silicones to impart improved combing and sensory properties. Cassia gum can be modified to generate cationic galactomannans with various levels of cationic substitution (9). That modification produced two novel cationic cassia conditioning polymers, EX-906 and EX-1086, with cationic charge density levels of 3.0 mEq/g, and 1.7 mEq/g, respectively, available from Lubrizol Advanced Materials, Inc.). The INCI classification for these polymers is cassia hydroxypropyltrimonium chloride. The chemical structures for EX-906 and EX-1086 are represented in Figure 3.

The surfactants used in this study are sodium lauryl ether sulfate (SLES-3), sodium lauryl sulfate (SLS) and cocamidopropyl betaine (CAPB), all commercially available from Lubrizol Advanced Materials, Inc.

METHODS

Clarity measurements. The clarity of a formulation is measured in %T (% transmittance) at 420 nm by a Brinkmann PC 920 colorimeter. Clarity measurements are referenced against de-ionized water (clarity rating of 100%).

Hair tress washing procedure. Virgin European brown hair tresses (2.5 g per tress) are pre-washed with a surfactant (10 wt% sodium lauryl sulfate) and thoroughly rinsed. Two-in-one conditioning shampoos (0.25 g) prepared with the formulations of the design of experiments are applied to each hair tress and gently lathered for 1 minute with 40
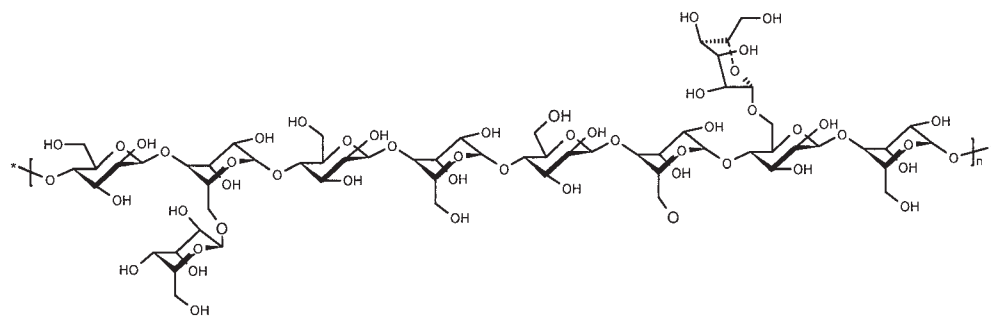

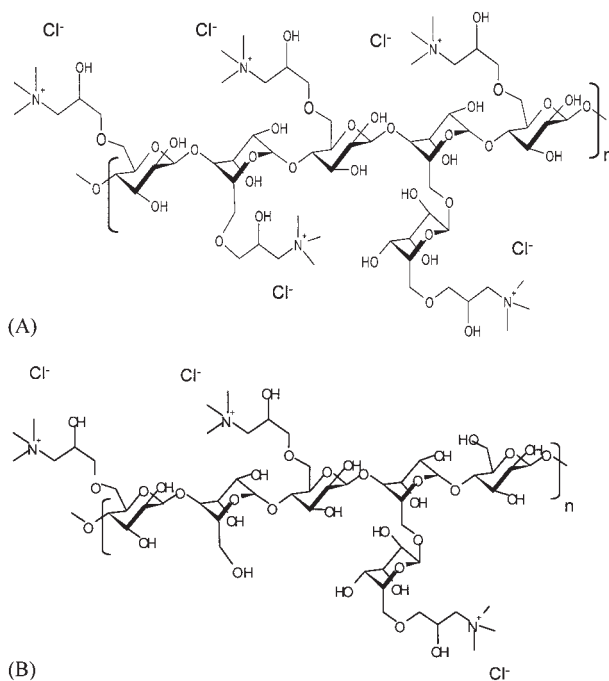**Figure 2.** Chemical structure of cassia gum.

Figure 3. Chemical structure of cationic cassia polymers EX-906 (3.0 mEq/g) (A) and EX-1086 (1.7 mEq/g) (B).

strokes and subsequently rinsed under flowing tap water (6.0 l/min) at $37° \pm 2°C$ for 30 seconds. The tresses are shampooed a second time and rinsed as previously described. After rinsing, the tresses are dried at $23° \pm 1°C$ and $50° \pm 5\%$ relative humidity.

Cationic polymer deposition on wool. Cationic polymer deposition is measured by using the Direct Red 80 dye colorimetric test (10). The cationic polymer deposition on a virgin wool swatch was studied after two washes, using the washing procedure previously described. Three wool swatches per experimental shampoo are washed two times with 0.25 g of shampoo, immersed into a dilute solution of Direct Red 80 dye for one minute and rinsed copiously to remove all excess dye. The intensity of red coloring (a*) is measured with a spectrophotometer (Labscan XE, HunterLab). Three readings per wool swatch are recorded.

Silicone deposition measurement. The relative amount of silicone (silicon atoms) deposited on Virgin European brown hair tress samples from a two-in-one shampoo composition is measured by X-Ray fluorescence (XRF) spectroscopy (11). A wavelength dispersive XRF spectrometer (PANalytical Axios Advanced Sequential 4kW spectrometer – Model Number PW4400) interfaced with a SuperQ 4 software application and fitted with a rhodium tube with an InSb crystal utilized to facilitate high sensitivity detection of silicon corresponding to the Si K alpha band. The samples are analyzed using a qualitative program to measure intensities across a two-theta scan range from 139.75° to 147.99° with a peak maximum at 144.53°. The samples are scanned in a vacuum environment using a tube voltage of 25 kV and a current of 160mA. The scanning speed is $0.05°.s^{-1}$. X-rays from the instrument excite silicon atoms deposited on the surface of the hair tress causing them to emit energy and fluoresce. The silicone fluorescence is detected and

recorded as counts per second. Samples for XRF analysis are prepared by cutting each treated hair tress into 1.5-cm lengths and placing the cut lengths into a sample cup having a 6-μm thick polyethylene support substrate formed into the bottom. A polyethylene spacer is placed on each cut tress to hold it onto the substrate. Three tresses per formulation are measured.

Sensory panel testing. Two-in-one conditioning shampoo formulations are compared by a trained panel (at least three panelists) for conditioning attributes using a forced choice test design between two treated hair tresses. Hair tresses treated with a conditioning shampoo formulation (Formulation A) are compared to hair tresses treated with another shampoo formulation (Formulation B). Each panelist is asked to indicate which tress performs better for each of five sensory attributes evaluated in comparing the two test formulations on the treated hair tresses. The sensory attributes evaluated by the panel include ease of wet combing, wet feel (soft feel or wet conditioned feel), ease of dry combing, dry feel (soft feel or dry conditioned feel) and static buildup (flyaway). The test protocol utilizes a matrix design of six treated tresses (three replicates for each of test Formulations A and B). The test matrix allows for the direct blind comparison of the 3 replicate treated tresses of Formulation A versus the 3 replicate treated tresses of Formulation B. By permutation of the 3 replicate treatments for each of Formulations A and B, nine comparisons of paired tresses (Formulation A versus Formulation B) are possible. The matrix is designed such that duplicate evaluations are included from the panel members. A total of 36 comparisons are carried out with the matrix design. A statistical analysis (Z-value calculation by exact binomial test, of preference of Formulation A versus Formulation B) is used to determine the level of confidence that Formulation A is statistically different (better or worse for the selected sensory attribute) from Formulation B.

Formulations. Each shampoo formulation contains surfactant levels as described in the design of experiments in Figure 1. The formulations also contain a fixed amount of NaCl at 1.0 wt% and fixed amount of cationic polymer (either EX-906 or EX-1086) at 0.25 wt%. The pH is adjusted with citric acid to pH =7 in all cases. For the silicone deposition and sensory performance analyses, 2 wt% of Dow Corning® 2-1352 silicone emulsion (0.5 μm) is added to the formulation. All wt% values indicated in this study are based on an active content.

RESULTS AND DISCUSSION

COACERVATION PROFILES

The coacervation profiles are recorded by measuring the change of formulation clarity with dilution ranging from 0 to 30 for each stable formulation. The coacervation curves generated for the various surfactant blend compositions with each cationic cassia polymer are found in Figures 4 and 5. The results show that the surfactant composition has a strong influence on the coacervation profiles. The coacervation profiles of both cationic cassia polymers can be extended to higher dilution range by changing the amount of SLES-3, SLS or CAPB. Consequently, the amount of coacervate formed over a dilution of 0 to 30 varies greatly. This amount can be quantified by integrating the area contained between the curves and the 100% transmittance horizontal line. The area is calculated by trapezoid numerical integration from dilution 0 to 30 and is reported as the calculated coacervation area in Table I and Table II.
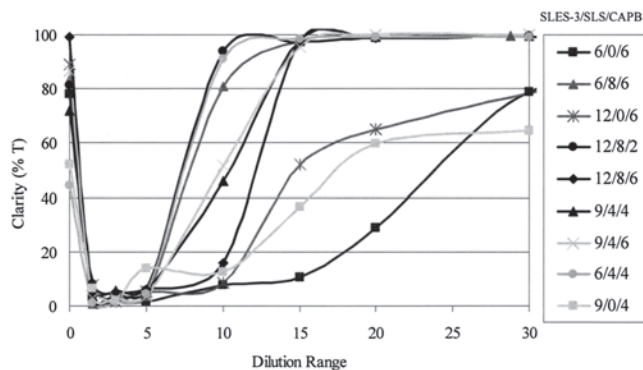
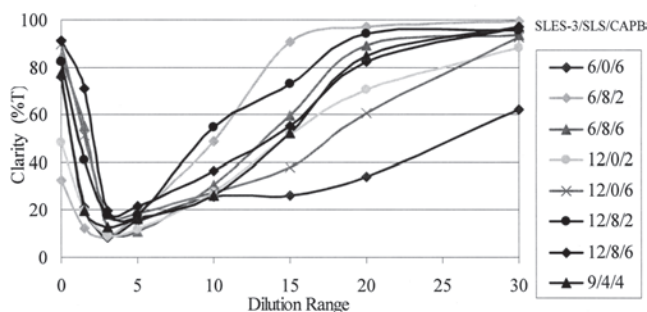**Figure 4.** Coacervation profiles for EX-906 (3.0 mEq/g).

Figure 5. Coacervation profiles for EX-1086 (1.7 mEq/g).

DEPOSITION RESULTS

Silicone deposition on European brown hair and the cationic polymer deposition on wool swatch were measured for both cassia polymers. The average results for the net silicon intensity for EX-906 for various surfactant blends and various amount of coacervate formed is reported in Figure 6. The results show that the amount of silicone deposited on the hair varies largely with the surfactant blend composition, and little correlation is observed between the amount of silicone deposited on the hair and the amount of coacervate formed. Higher amounts of coacervate formation (i.e., by broadening of the coacervation profile to higher dilution range) do not lead to higher level of silicone deposition. This result is unexpected as literature results indicate that the formation of higher amounts of coacervate of broadening of coacervation profiles leads to higher silicone deposition (12,13).

The cationic polymer deposition on wool was measured by Direct Red 80 dye titration by spectrophotometry as previously described. The results for EX-906 are summarized in Figure 7 and show only a slight change in the amount of cationic cassia polymer deposited on the wool with different surfactant blend compositions. As similarly seen in the silicone deposition results, there is no correlation between the amount of cationic cassia polymer deposited on wool and the amount of coacervate formed with the various surfactant blend compositions. The correlation between the EX-906 cationic cassia deposition on wool and the silicone deposition on hair is illustrated in Figure 8. The data show that there is a relatively good correlation between the cationic cassia EX-906 polymer deposition

Table I
Calculated Coacervate Area per Surfactant Blend Composition for EX-906 (3.0 mEq/g)

SLES-3 amount (wt%)	SLS amount (wt%)	CAPB amount (wt%)	Calculated coacervate area
6	0	6	247
6	8	6	55
12	0	6	196
12	8	2	43
12	8	6	88
9	4	4	59
9	4	6	65
6	4	4	53
9	0	4	184

Table II
Calculated Coacervate Area per Surfactant Blend Composition for EX-1086 (1.7 mEq/g)

SLES-3 amount (wt%)	SLS amount (wt%)	CAPB amount (wt%)	Calculated coacervate area
6	0	6	212
6	8	2	49
6	8	6	86
12	0	2	116
12	0	6	125
12	8	2	55
12	8	6	88
9	4	4	93

and the silicone deposition. High silicone deposition generally corresponds to high cationic polymer deposition from the same surfactant mixture.

A similar systematic study was also performed for the low charge density cationic cassia polymer (EX-1086). The trends are very similar to those observed for the high cationic charge density cassia polymer. The data for the net silicon intensity for EX-1086 for various
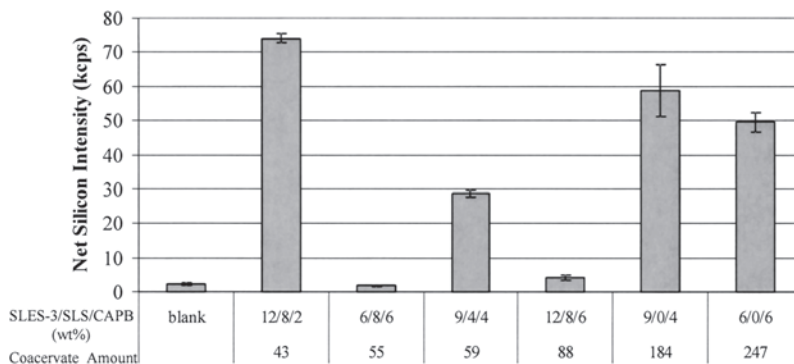

Figure 6. Silicone deposition measured by XRF for EX-906 (3.0 mEq/g). The error bars represent ± one standard deviation.
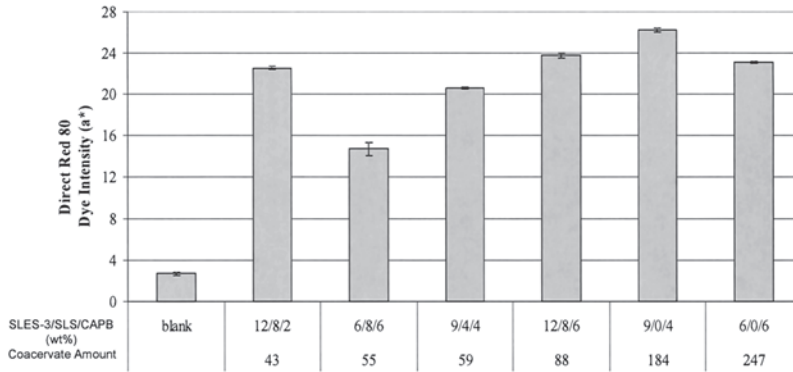
Figure 7. Cationic polymer deposition for EX-906 (3.0 mEq/g). The error bars represent ± one standard deviation.
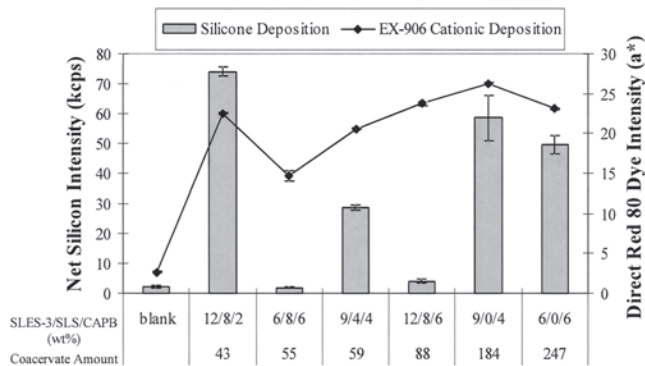

Figure 8. Correlation between silicone and cationic deposition for EX-906 (3.0 mEq/g). The error bars represent ± one standard deviation.

surfactant blends and various amounts of coacervate formed are reported in Figure 9. Once again, the results show that the amount of silicone deposited on the hair varies largely with the surfactant blend composition and little correlation is observed between the amount of silicone deposited on the hair and the amount of coacervate formed by the various surfactant blends. Higher amounts of coacervate formation (or a broadening of the coacervation profile to higher dilution range) do not lead to higher levels of silicone deposition for EX-1086, as similarly seen for EX-906.

EX-1086 deposition on wool results are summarized in Figure 10 and show only a slight change in the amount of cationic cassia polymer deposited on the wool with variation of the surfactant package and, as similarly seen in the silicone deposition results, there is no correlation between the amount of cationic cassia polymer deposited on wool and the amount of coacervate formed with the various surfactant blend compositions. The correlation between the EX-1086 cationic cassia deposition on wool and the silicone deposition on hair is illustrated in Figure 11. The data show that there is not a strong correlation between the cationic cassia polymer deposition and the silicone deposition with the surfactant blend compositions studied here. A relatively constant level of cationic cassia deposition is obtained with corresponding varying degrees of silicone deposition (high or low) depending on the surfactant mixtures.
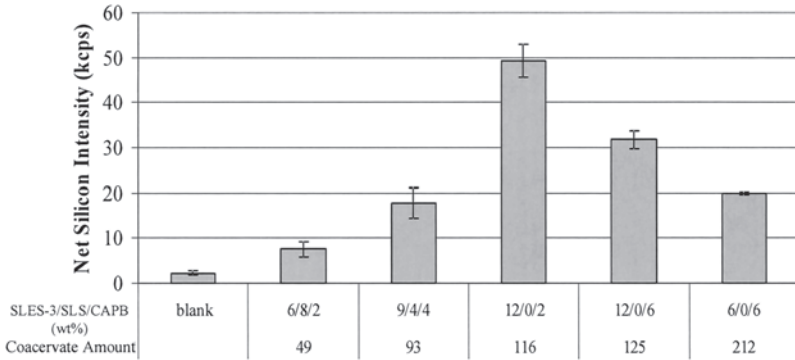
Figure 9. Silicone deposition measured by XRF for EX-1086 (1.7 mEq/g). The error bars represent ± one standard devation.
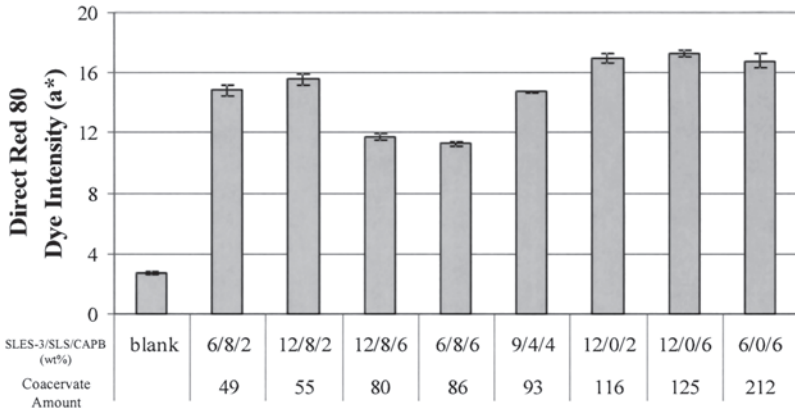

Figure 10. Cationic deposition of EX-1086 (1.7 mEq/g). The error bars represent ± one standard deviation.
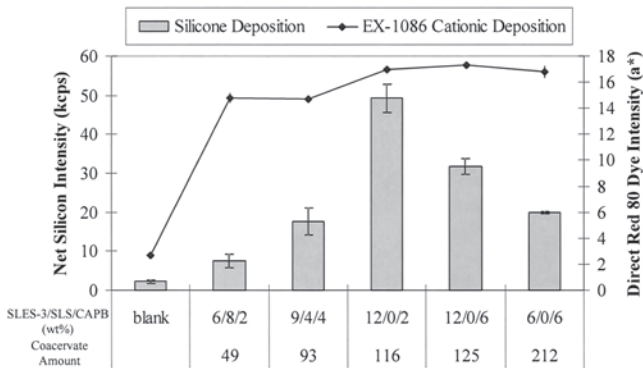

Figure 11. Correlation between silicone and cationic deposition for EX-1086 (1.7 mEq/g). The error bars represent ± one standard deviation.

SENSORY PANEL RESULTS

Surfactant blend formulations with varying coacervation profiles are selected and compared with sensory panel testing on virgin European brown hair to determine if the

coacervate profile influences the sensory performance on hair. Several shampoo formulation from the design reported in Figure 1 are compared for sensory performance. The shampoo formulation also contains 0.25 wt% cationic cassia polymer (EX-906 or EX-1086), 2 wt% of a small particle size dimethicone silicone emulsion (Dow Corning® 2-1352 silicone emulsion (0.5 μm average particle size)), and 1 wt% NaCl; it is adjusted to pH of 7. An example of shampoo formulations used in a sensory panel test is shown in Table III.

As previously described, several criteria were compared as a forced choice between hair tress pairs. The sensory panel tests results are analyzed for statistical significance using an exact binomial test, and only the results at 95% and 99% confidence levels are reported. An example of the statistical analysis results from the comparison of formulation A to formulation B from Table III is reported in Figure 12. Statistically superior wet combing (at more than 99% confidence level), wet feel (at more than 99% confidence level), dry combing (at more than 99% confidence level), and dry feel (at more than 95% confidence level) are achieved with formulation B. No statistically significant difference in static buildup is observed between the two formulations. These results also show that although both formulations show relatively similar coacervation profiles (similar coacervate amount as reported in Table I), they demonstrate a significant conditioning performance difference.

Table III
Formulation A and B Composition Used for a Sensory Panel Test (all wt% active)

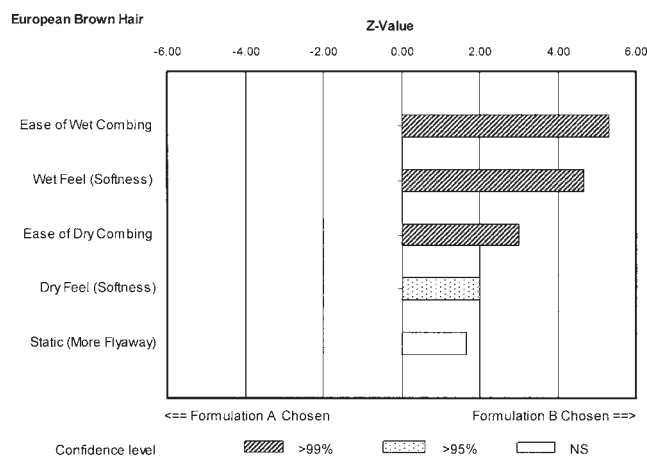|	Formulation A	Formulation B
SLES-3	6	9
SLS	8	4
CAPB	6	4
Silicone emulsion, Dow Corning® 2-1352 (0.5 μm)	2	2
Cationic cassia polymer EX-906	0.25	0.25
NaCl	1	1

Figure 12. Statistical analysis of sensory panel testing.

Several panel sensory testing comparisons of varied surfactant blend compositions are performed in a similar manner, and the results are summarized in Table IV for EX-906 formulations and in Table V for EX-1086 formulations. Each table describes the surfactant combination used (amounts of SLES-3, SLS and CAPB) in the shampoo formulation, the coacervate amount calculated for each surfactant blend, the amount of silicone deposited on the hair (i.e., the net silicon intensity in kcps) and the statistical analyses results from each panel comparison.

The results show that for both EX-906 and EX-1086, sensory performance is highly correlated to the amount of silicone deposited on hair (i.e., the net silicon intensity) and not to the amount of coacervate formed. Conditioning sensory performance is highly influenced by the surfactant blend composition and is well predicted by the measurement of silicone deposited on the hair.

SURFACTANT BLEND CHARACTERIZATION

As previously discussed, the surfactant blends used in combination with the cationic cassia polymers in this study have a strong influence on the amount of coacervate formed upon

Table IV
Sensory Panel Results for EX-906 (3.0 mEq/g)

SLES-3/SLS/CAPB (wt%)		SLES-3/SLS/CAPB (wt%)		
Coacervate amount	Net Si intensity (kcps)	Coacervate amount		Net Si intensity (kcps)
6/0/6		12/8/2		
247	49	43		74
		Better dry combing (99% CL)*		
		Better dry feel (95% CL)		
9/0/4		12/8/2		
184	58	43		74
Better wet combing (99% CL)				
12/8/6		12/8/2		
88	4	43		74
		Better wet combing (99% CL)		
		Better wet feel (99% CL)		
		Better dry combing (99% CL)		
		Better dry feel (99% CL)		
		Less static (95% CL)		
6/8/6		9/4/4		
55	2	59		29
		Better wet combing (99% CL)		
		Better wet feel (99% CL)		
		Better dry combing (99% CL)		
		Better dry feel (99% CL)		

*CL = Confidence level.

Table V
Sensory Panel Results for EX-1086 (1.7 mEq/g)

SLES-3/SLS/CAPB (wt%)		SLES-3/SLS/CAPB (wt%)	
Coacervate amount	Net Si intensity (kcps)	Coacervate amount	Net Si intensity (kcps)
6/0/6		6/8/2	
212	20	49	7
Better wet combing (99% CL*)			
Better wet feel (99% CL)			
Better dry combing (99% CL)			
Better dry feel (99% CL)			
12/0/6		6/8/2	
125	32	49	7
Better wet combing (99% CL)			
Better wet feel (99% CL)			
Better dry combing (99% CL)			
12/0/2		9/4/4	
116	49	93	18
Better wet combing (99% CL)			
Better wet feel (99% CL)			
Better dry combing (99% CL)			
Better dry feel (99% CL)			
9/4/4		6/8/2	
93	18	49	7
Better wet combing (99% CL)			
Better wet feel (99% CL)			

*CL = Confidence level.

dilution, the amount of silicone and cationic cassia deposited on the hair, and consequently, on the sensory performance. The surfactant blends can be further characterized with some simple concepts such as aspect ratio and micelle charge. Both charge on the surfactant micelles and the amount of surfactant are important variables to consider in attempting to understand performance. These two parameters can be estimated directly from the formulation. The relations are as follows (all wt% values indicated are based on an active content):

$$\text{Micelle charge} : \frac{\text{Total surfactant charge (mol)}}{\text{Total surfactant amount (mol)}} \tag{1}$$

$$\text{Total surfactant charge} = \frac{\text{wt\% SLS}}{288} + \frac{\text{wt\% SLES3}}{421} \tag{2}$$

$$\text{Total surfactant amount} = \frac{\text{wt\% SLS}}{288} + \frac{\text{wt\% SLES3}}{421} + \frac{\text{wt\% CAPB}}{343} \tag{3}$$

It is important to note that the micelles are made up of mixtures of all of the surfactants that are in the shampoo. In fact, it is commonly assumed that the relative amount of each surfactant in a micelle is the same as in the bulk formulation. This means that the average surfactant charge is a convenient measure of the potential that would exist on each micelle. Thus, it will be considered to be a theoretical measure of micelle charge density. The relative sizes of the micelles can be estimated from the viscocity of the shampoos itself. Since the micelles primarily increase in one dimension, a convenient description of micelle size is aspect ratio. This terminology will be used here. An estimate of this value has been obtained in previous work (14) by modeling the change of the Brookfield viscosity measured at 20rpm with the various surfactant blend composition (in terms of SLES-3, CAPB and SLS content) and Equation 4 summarizes the modeling fit.

$$\text{Aspect ratio} = \text{wt\% CAPB} + 0.8 * \text{wt\% SLS} + 0.15 * \text{wt\% SLES - 3}$$
$$+ \ 0.15 * (\text{wt\% SLS - 2.1}) * (\text{wt\% CAPB - 4.1}) \tag{4}$$

This measure of aspect ratio is not a pure one. It is partially confounded with the amount of surfactant that is in the formulation as well as the amount of salt. Thus, it should be only considered as a rough estimate of size. These factors will be used to rationalize performance.

For the silicon deposition data presented above, the micelle aspect ratio and total micelle charge were calculated for each surfactant blend. The ratio of aspect ratio to micelle charge against the total silicone deposition for each cationic cassia polymer is plotted in Figures 13 and 14. It can be seen from the P value in Figure 13 that in the case of the higher cationic charge cassia polymer, there is a relatively high confidence level (98%) that these factors are important in explaining silicone deposition. The results show that as the ratio of the aspect ratio to micelle charge increases, the silicone deposition with EX-906 decreases, i.e. the conditioning performance decreases. The ratio shown is an indirect measure of the inverse of micelle charge density (as the micelle charge density increases, the silicone deposition increases). Thus, the data show that micelles having a
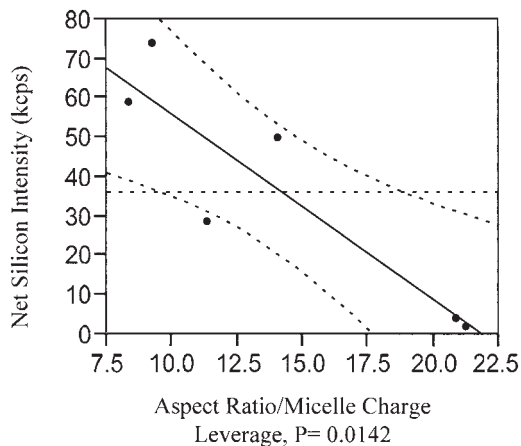

Figure 13. Correlation of silicone deposition with the ratio of aspect ratio to micelle charge for EX-906 (3.0 mEq/g).
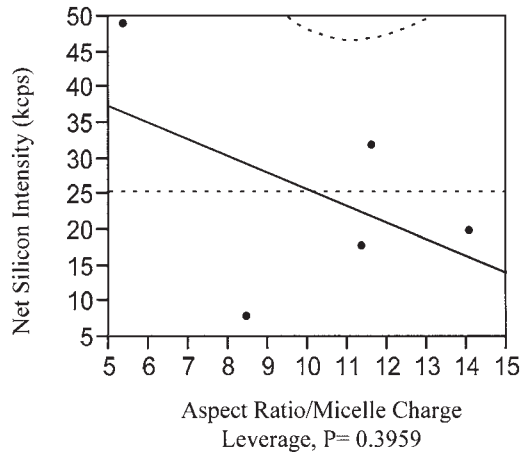
Figure 14. Correlation of silicone deposition with the ratio of aspect ratio to micelle charge for EX-1086 (1.7 mEq/g).

high charge density (either through a small aspect ratio or high charge or both) provide a favorable environment for interaction with the higher cationic charge cassia polymer and lead to higher silicone deposition and superior conditioning performance.

The effects of the nature of the interaction of high charge density micelles with the higher charge density cationic cassia polymer EX-906 are not well understood. Several explanations are possible. The complex may be more likely to adhere better to the negatively charged hair surface due to better neutralization of the high cationic charge polymer with the high charge micelles or the flocculation may be more efficient between EX-906 and highly negatively charged micelles to entrap the silicone. It is also possible that there is a different interaction (or conformation) between EX-906 and highly charged micelles compared to micelles with high aspect ratio (rod-like) or lower charge.

The ratio of aspect ratio to micelle charge for the lower charge density cationic cassia polymer EX-1086 is plotted against the total silicone deposition and shown in Figure 14. In this case, it is seen that there is not a significant correlation (P values of 0.39) between the silicone deposited on the hair and the ratio of aspect ratio to micelle charge. The mechanism for optimizing the conditioning performance with the lower cationic charge density cassia polymer appears to be different from the higher cationic charge density cassia polymer. Extension of the coacervation curve (the latter part of coacervation curve after dilution 10) may help to enhance performance of EX-1086 but not EX-906. Thus, forming as much coacervate over as wide of a dilution range as possible may lead to better performance. It is hypothesized that an inherent lack of adhesion or poorer flocculation of the coacervate formed by EX-1086 will lead to lesser deposition. This could then be compensated by a higher amount of coacervate.

The silicone deposition data for both EX-906 and EX-1086 can be merged and modeled together if the charge on the cationic polymer is taken into account. This is done as shown in Figure 15. The overall effects of the parameters show that a greater aspect ratio decreases silicone deposition and a greater charge on the cationic cassia polymer increases it.
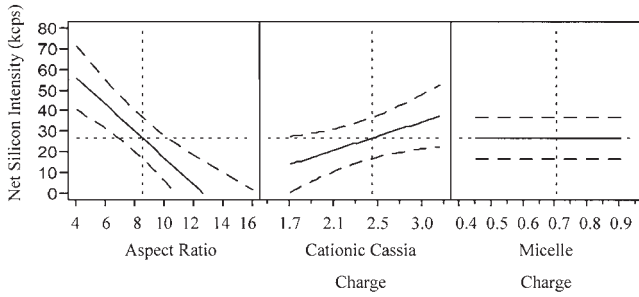
Figure 15. Silicone deposition prediction for EX-906 and EX-1086.

On the other hand, an increase in the micelle charge does not seem to have a strong impact on the silicone deposition. Further analysis considers the interaction profiles shown in Figure 16. The profiles show a strong interaction between the cationic charge density of the cassia polymers and the micelle charge density. It is seen from this analysis that the average charge on the surfactants (micelle charge) is important in determing silicone deposition and, specifically, that a higher charge produces more deposition for the higher cationic charge cationic cassia polymer but less silicone deposition for the lower cationic charge cassia polymer. It is further seen in the main effects as well as the interactions that a higher aspect ratio decreases silicone deposition.

The effect of the ratio of aspect ratio to micelle charge on the cationic deposition of either EX-906 or EX-1086 is reported in Figure 17. As observed for the silicone deposition, the ratio of the micelle aspect ratio and micelle charge has an effect on the cationic polymer deposition on wool. The amount of cationic polymer deposited on wool after 2 washes decreases as the aspect ratio to micelle charge ratio increases.
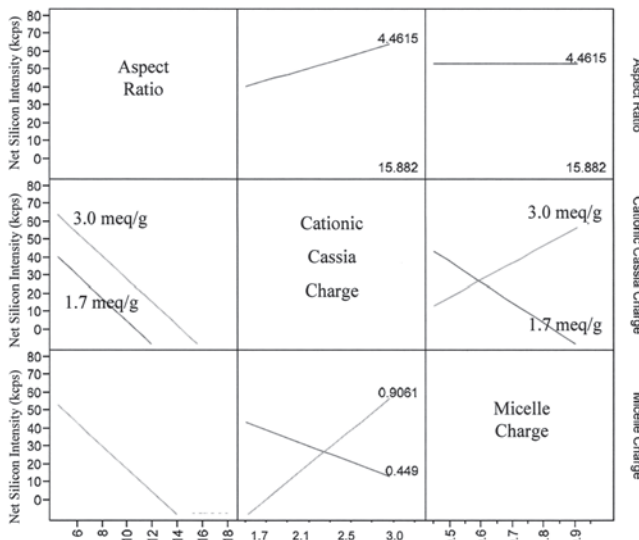

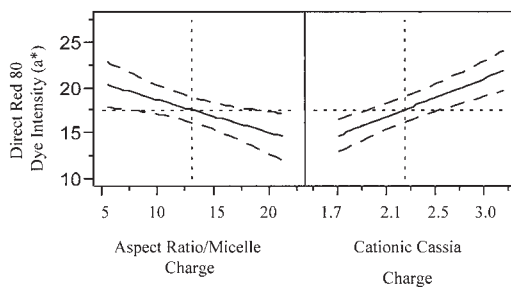**Figure 16.** Interacion parameters for EX-906 and EX-1086.

Figure 17. Correlation of cationic deposition with the ratio of aspect ratio to micelle charge for EX-906 and EX-1086.

CONCLUSIONS

The results clearly demonstrate that, contrary to what was previously assumed, the extension of coacervation profiles to a higher dilution range for formulations containing a more highly charged cationic polymer does not lead to improved conditioning performance. Other factors besides the shape of the coacervation curve influence the conditioning performance of cationic cassia polymers on European brown hair. Even so, the formulation of the surfactant composition has a strong influence on the cationic polymer performance and the silicone deposition is a primary determinant of the conditioning sensory performance. Three parameters are proposed to be of importance in determining silicone and cationic polymer deposition: cationic cassia polymer charge density, average surfactant charge (micelle charge) and total amount of surfactant (aspect ratio). Sensory hair panel testing, silicone and cationic polymer deposition results can be predicted to a very high confidence level using models that incorporate these three factors. There appear to be several mechanisms that are of importance in determining silicone deposition and, therefore, sensory performance. Which of these is operative depends on the cationic polymer charge density. Silicone deposition data as well as sensory panel tests both indicate that for a more highly charged polymer, either the adhesion of the polymer-surfactant complex to the hair and/or its ability to flocculate the silicone is the determining factor, whereas with a lower cationically charged polymer, the amount of complex formed is more important.

ACKNOWLEDGMENTS

REFERENCES

(1) R. Y. Lochhead, Conditioning shampoo, *Soap Cosmet. Chem. Spec.,* 42–49 (1992).
(2) E. D. Goddard, "Polymer/Surfactant Interactions in Applied Systems," in *Principles of Polymer Science and Technology in Cosmetics and Personal Care,* E. D. Goddard and J. V. Grubber, Eds. (Marcel Dekker, New York, 1999), pp. 181–215.
(3) P. Hossel, R. Dieing, R. Norenberg, A. Pfau, and R. Sander, Conditioning polymers in today's shampoo formulations—Efficiency, mechanisms and tests methods, *Int. J. Cosmet. Sci.,* **22**(1), 1–10 (2000).

(4) P. Dubin and R. Oteri., Association of polyelectrolytes with oppositely charged mixed micelles, *J. Colloid Interfacial Sci.,* **95**(2), 453–461 (1983).

(5) J. A. Faucher and E. D. Goddard, Influence of surfactants on sorption of a cationic polymer by keratinous substrate, *J. Colloid Interface Sci.,* **55,** 313–319 (1976).

(6) W. Li. and S. L. P. Jordan, Cationic cellulosic polymers with multifunctional and outstanding performances for personal care, *Cosmet. Toiletr. Manufac. Worldwide,* 1–4 (2003).

(7) S. Chiron, Performance and sensory benefits of cationic guar in hair care applications, *Cosmet. Toiletr.,* **119**(2), 47–51 (2004).

(8) M. Gamez-Garcia, Polycation substantivity to hair, *IFSCC,* **4**(2), 99–107, (2001).

(9) F. Utz *et al.,* Cationic cassia derivatives and applications therefore, *US Patent 7,262,157 B2* (2007).

(10) R. J. Crawford and C. R. Robbins, A replacement for Rubine dye for detecting cationics on keratin, *J. Soc. Cosmet. Chem.,* **31,** 273–278 (1980).

(11) J. V. Gruber, B. R. Lamoureux, N. Joshi, and L. Moral, The use of X-ray fluorescence spectroscopy to study the influences of cationic polymers on silicone oil deposition from shampoo, *J. Cosmet. Sci.,* **52,** 131–136 (2001).

(12) J. V. Gruber, B. R. Lamoureux, N. Joshi, and L. Moral, Influence of cationic polysaccharides on polydimethyl siloxane (PDMS) deposition onto keratin surfaces from a surfactant emulsified system, *Colloids Surf. B,* **19,** 127–135 (2000).

(13) T. V. Drovetskaya, E. F. Diantonio, R. L. Kreeger, J. L. Amos, and D. P. Frank, Newly high charge density hydrophobically modified cationic HEC polymers for improved co-deposition of benefit agents and serious conditioning for problem hair, *J. Cosmet. Sci.,* **58**(4), 421–434 (2007).

(14) C. Lepilleur, E. Schiferl, J. Mullay, P. McCalister, C. Kyer, and T. Clifford, Unpublished Lubrizol internal technical report (2009).