

Use of statistical modeling to predict the effect of formulation composition on conditioning shampoo performance

CAROLE LEPILLEUR, ANN GIOVANNITTI-JENSEN,
and CAROL KYER, *Lubrizon Advanced Materials Inc., Personal and
Home Care, Brecksville, OH 44141.*

Accepted for publication May 13, 2013

Synopsis

Formulation composition has a dramatic influence on the performance of conditioning shampoos. The purpose of this study is to determine the factors affecting the performance of various cationic polymers in those systems. An experiment was conducted by varying the levels of three surfactants (sodium lauryl ether sulfate, sodium lauryl sulfate, and cocamidopropyl betaine) in formulations containing various cationic polymers such as cationic cassia derivatives of different cationic charge densities (1.9, 2.3, and 3.0 mEq/g), cationic guar (0.98 mEq/g), and cationic hydroxyethyl cellulose (1.03 mEq/g). The results show the formulation composition dramatically affects silicone and cationic polymer deposition. In particular, three parameters are of importance in determining deposition efficiency: ionic strength, surfactant (micelle) charge, and total amount of surfactant. The cationic polymer composition, molecular weight, and charge density are also important in determining which of the previous three parameters influence the performance most.

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 on dilution with water. The literature suggests that on shampoo application, foaming, washing, and rinsing, such cationic polymers form a complex with anionic and amphoteric surfactants that phase separate from the bulk solution. This phase separation, or coacervation, is also known as the “Lochhead effect” (1). Phase separation on dilution has been explained in the literature by the coulombic attraction between the anionic function of the surfactant and the cationic groups of the polymer. Goddard (2) described that at low surfactant concentration [below the critical micelle concentration (CMC)] anionic surfactants condense on the polycations. The resulting ion pairs convert

Address all correspondence to Carole Lepilleur at Carole.Lepilleur@lubrizol.com.

This paper was presented at the fifth International TRI/Princeton Conference on Applied Hair Science, September 20–21, 2012.

the cationic sites into hydrophobe-substituted sites. Hydrophobic interactions within and between the polycations cause 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 blend used in the formulation, the ionic strength, pH, and temperature. For instance, the molecular weights of the 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 (6).

The objective of this study is to determine the effect of the surfactant formulation composition on the conditioning performance of various cationic polymers. A previous study (7) showed that three parameters are of importance in determining silicone deposition of cationic cassia polymers: polymer charge, surfactant micelle charge (i.e., the amount of anionic content in the surfactant micelle), and total amount of surfactant. However, the study also showed that the effects of the total amount of surfactant and ionic strength were confounded. A new design of experiments, as illustrated in Figure 1, was developed to unconfound these factors by considering the influence of micelle charge, amount of surfactant, and ionic strength independently. The design was also expanded to include different cationic polymers: a cationic cassia polymer of a mid-range cationic charge density (2.3 mEq/g) in addition to the cationic cassia polymers of reference 7, which have

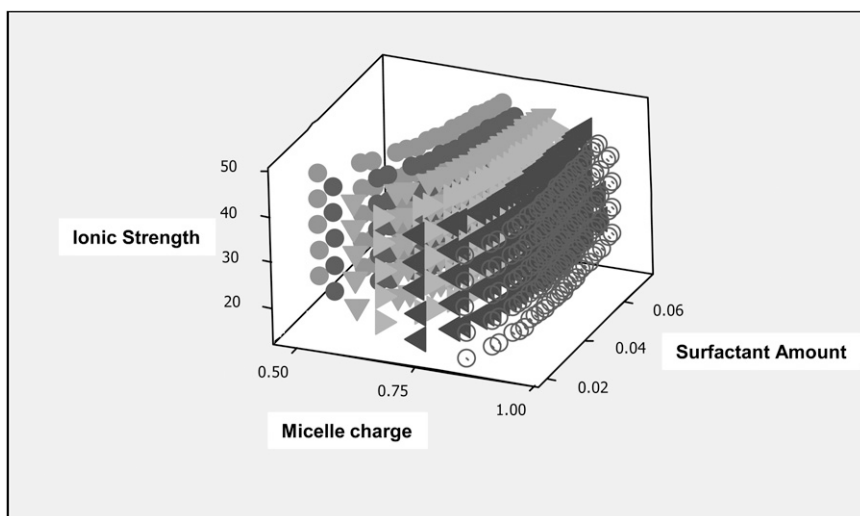


Figure 1. New design space for shampoo formulations with various micelle charge (mole fraction), ionic strength (in S/m), and surfactant amount (in mol). The various symbols represent curved surfaces of the overall design space. Each symbol represents a possible formulation composition for the design.

cationic charge densities of 1.9 and 3.0 mEq/g, and widely used commercially available cationic polymers such as cationic guar polymer (0.98 mEq/g) and cationic hydroxyethyl cellulose, polyquaternium-10 (PQ-10; 1.03 mEq/g). Latter two polymers are chosen because of their extensive use as conditioning polymers in shampoos. This study covers a wide range of polymer compositions (galactomannans and cellulose), molecular weights, and cationic charge densities.

It is known that the formulation composition has a dramatic effect on physical properties (viscosity, clarity, and turbidity) and also on the coacervation behavior (7–9). The purpose of this study is to determine the factors influencing the conditioning performance of shampoos, specifically the deposition of a small-particle-size silicone emulsion (average silicone droplet size of about 0.5 μm) and cationic polymer deposition.

EXPERIMENTAL

MATERIALS

Various cationic polymers such as cationic cassia derivatives of different cationic charge densities (1.9, 2.3, and 3.0 mEq/g), cationic guar (0.98 mEq/g), and cationic hydroxyethyl cellulose (1.03 mEq/g) are used in this study as illustrated in Table I. 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 gum can be modified to generate cationic galactomannans with various levels of cationic substitution (10). The modification produces cationic cassia conditioning polymers, CC1.9, CC2.3, and CC3.0, with cationic charge density levels of 1.9, 2.3, and 3.0 mEq/g, respectively, available from Lubrizol Advanced Materials (Brecksville, OH). The chemical structures of the various cationic polymers used in this study are 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 having a mannose to galactose ratio of about 2, have been successfully used in conditioning shampoos in combination with silicones to impart improved combing and sensory properties. The International Nomenclature of Cosmetic Ingredients designation for the cationic cassia polymers is cassia hydroxypropyltrimonium

Table I
Cationic Polymer Characterization

Cationic polymer	Code name	Charge density (mEq/g)	Molecular weight Mw (D)
Cationic cassia	CC1.9	1.9	600,000
Cationic cassia	CC2.3	2.3	600,000
Cationic cassia	CC3.0	3.0	600,000
Cationic guar	CG0.98	0.98	2,000,000
Cationic hydroxyethyl cellulose	PQ-10 1.03	1.03	400,000

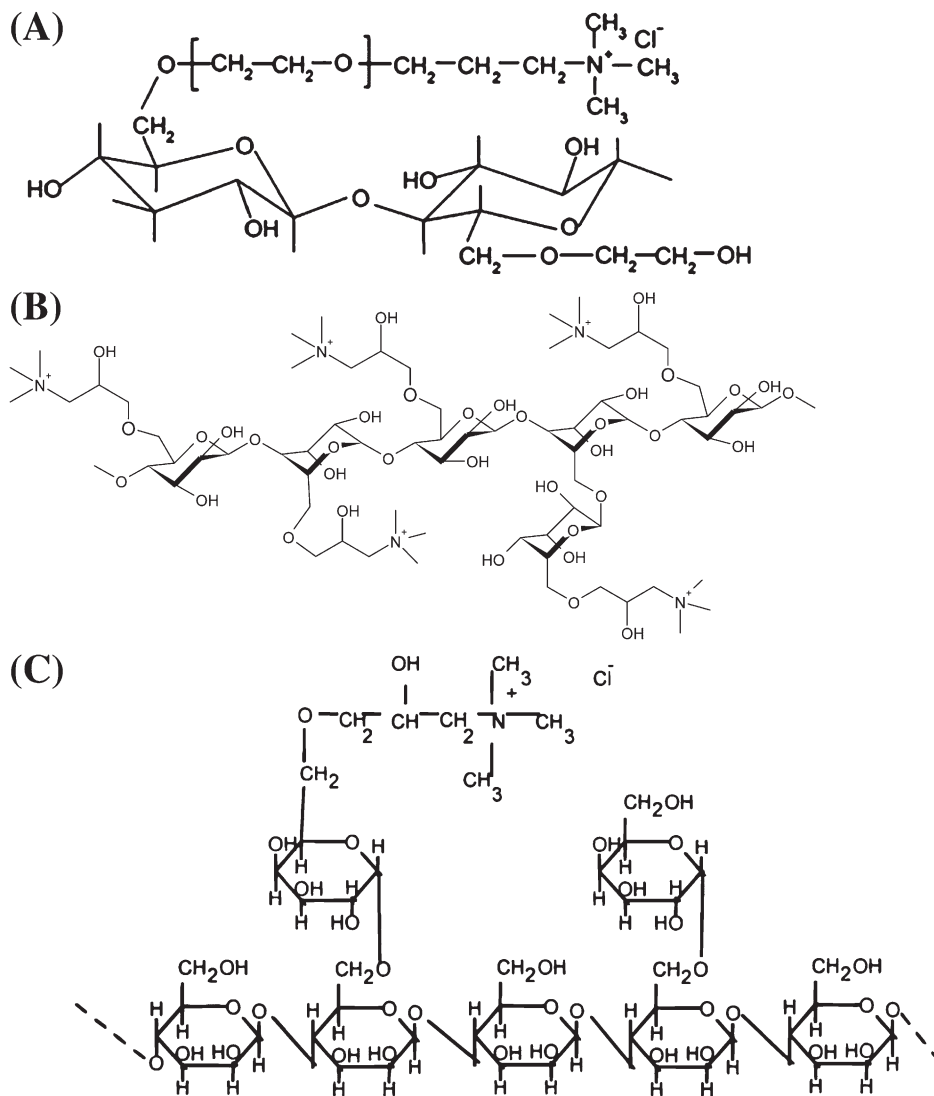


Figure 2. Chemical structures of (A) cationic hydroxyethyl cellulose, (B) cationic cassia, and (C) cationic guar.

chloride, for cationic guar is guar hydroxypropyltrimonium chloride, and for cationic hydroxyethyl cellulose polymer is polyquaternium-10. The molecular weight of the cationic polymer can be determined by a low-angle light-scattering detector (Triple Detector Array, available from Viscotek (Houston, TX), model number 302-040) coupled with two Visco-Gel C-MBHMW-3078 columns using a sample concentration of 0.6 mg/ml in a 0.05 M ammonium acetate/10% methanol solvent (at a pH of 4.0), an injection volume of 100 μ l, a column temperature of 30°C, and a flow rate of 0.9 ml/min.

The surfactants used in this study are sodium lauryl ether sulfate (SLES-2), sodium lauryl sulfate (SLS), and cocamidopropyl betaine (CAPB), all commercially available

from Lubrizol Advanced Materials. The dimethicone emulsion [Dow Corning® 2-1352 silicone emulsion (0.5 μm mean particle size)] available from Dow Corning (Midland, MI) was used. The cationic guar and cationic hydroxyethylcellulose polymers (PQ-10) are commercial products available from Rhodia (Cranbury, NJ) and Dow Chemical (Midland, MI), respectively.

METHODS

Hair tress washing procedure. Virgin European brown hair tresses (2.5 g per tress) are pre-washed with an aqueous surfactant solution (10 wt% SLS) and thoroughly rinsed. Two-in-one conditioning shampoos prepared with the formulations of the design of experiments are applied (0.5 g) to each hair tress and gently lathered for 1 min with 40 strokes and subsequently rinsed under flowing tap water (3.8 l/min) at $37 \pm 2^\circ\text{C}$ for 30 s. The tresses are shampooed a second time and rinsed as previously described. After rinsing, the tresses are dried at $23 \pm 1^\circ\text{C}$ 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 (11). The cationic polymer deposition on a virgin wool muslin swatch was measured after two washes, using the washing procedure previously described. Three wool swatches per experimental shampoo are washed twice with 0.25 g of shampoo, immersed into a dilute solution of Direct Red 80 dye for 1 min and rinsed copiously to remove all excess dye. The intensity of red coloring (a^*) is measured with a spectrophotometer (Labscan XE, HunterLab, H. F. Scientific, Fort Myers, FL). Three readings per wool swatch are recorded. Although this titration method is quite useful, the amount of cationic polymer deposited on the wool substrate and the polymer cationic charge density are confounded in the measure of a^* . So comparison of a^* values cannot be done among cationic polymers of various cationic charge densities.

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 (12,13). The instrumentation used is a wavelength dispersive XRF spectrometer (Axios Advanced Sequential 4 kW spectrometer, available from PANalytical (The Netherlands), model number PW4400) interfaced with a SuperQ 4 software application and fitted with a rhodium tube with an InSb crystal used 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 160 mA. The scanning speed is $0.05^\circ/\text{s}$. X-rays from the instrument excite silicon atoms deposited on the surface of the hair tress causing them to emit energy and fluoresce. The silicon 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 at the bottom. A polyethylene spacer is placed on each cut tress to hold it onto the substrate. Three tresses per formulation are measured.

Formulations. Each shampoo formulation contains surfactant levels described in the design of experiments in Table II. The formulations also contain a fixed amount of cationic polymer at 0.25 wt%. The pH is adjusted with citric acid to pH 5.8 in all cases. For silicone

Table II
Formulation Compositions Derived from the Design of Experiments Used for All Cationic Polymers

Formulation (wt%)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SLES-2	6	10	6	14	6	6	16	8	6	12	8	6	14	6
SLS	0	8	0	8	0	0	0	6	0	2	8	0	8	8
CAPB	1	6	1	1	3	6	1	1	6	1	6	3	1	1
NaCl	0	0	2	1.5	1	2	2	0.5	0	0.5	2	0	0	2
Cationic polymer	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25

deposition, 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 active content.

Experimental design. The new design space comprises several curved surfaces as represented by the different symbols shown in Figure 1. Formulations containing various micelle charge, surfactant amount, and ionic strength are derived from points selected from the curved surfaces of the design space. Each symbol represents a possible formulation composition for the design. The composition of these formulations are converted in terms of commonly used ingredients amounts such as SLES-2, SLS, CAPB, and sodium chloride contents as summarized in Table II.

Statistical analysis. The statistical analysis was performed using JMP® 10.0.2 software, available from S.A.S Institute Inc. (Cary, NC). Prediction profilers and interaction profiles are generated from the statistical models derived from the experimental design. A profile trace is the predicted response as one variable is changed while the others are held constant at the current values. The prediction profiler recomputes the profiles and predicted responses (in real time) as you vary the value of an X variable. Prediction profilers are especially useful in multiple-response models to help judge which factor values can optimize a complex set of performance criteria. There are several important points to note when interpreting a prediction profiler: the importance of a factor can be assessed to some extent by the steepness of the prediction trace. If the model has curvature terms, such as squared terms, then the traces may be curved. If you change a factor's value, then its prediction trace is not affected, but the prediction traces of all the other factors can change. The Y response line crosses the intersection points of the prediction traces with their current value lines. If there are interaction effects or cross-product effects in the model, the prediction traces can shift their slope and curvature as you change current values of other terms. If there are no interaction effects, the traces only change in height, not in slope or shape. The interaction profiler brings up interaction plots, which illustrate the joint effects of the factors on the response. Some examples on how to read these graphs can be found in reference 14.

RESULTS AND DISCUSSION

SURFACTANT BLEND CHARACTERIZATION

The surfactant blends can be characterized with simple concepts such as micelle charge, total surfactant amount, and ionic strength. Both micelle charge and the total surfactant amount are important variables to consider in attempting to understand performance.

These parameters can be calculated directly from the amounts of each ingredient in the formulation. The relations are as follows:

$$\text{Micelle charge} = \frac{\text{Total charged surfactant amount (mol)}}{\text{Total surfactant amount (mol)}}, \quad (1)$$

where

$$\text{Total charged surfactant amount} = \frac{\text{wt\% SLS}}{288} + \frac{\text{wt\% SLES-2}}{381} \quad (2)$$

$$\text{Total surfactant amount} = \frac{\text{wt\% SLS}}{288} + \frac{\text{wt\% SLES-2}}{381} + \frac{\text{wt\% CAPB}}{343}. \quad (3)$$

The micelle charge is a mole fraction; the total charged surfactant amount and total surfactant amount are expressed in moles. The ionic strength is the conductivity (in S/m) of the formulation.

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 exists on each micelle. Thus, it will be considered to be a theoretical measure of micelle charge density.

SILICONE DEPOSITION

Statistical models for silicone deposition were developed for each cationic polymer. The graphs of Figure 3 show the correlation between the actual silicone deposition value measured for each formulation by XRF on the y axis and the predicted silicone deposition value derived from the statistical models on the x axis. Overall, relatively good models were obtained for cationic cassia polymers, cationic guar, and cationic hydroxyethyl cellulose (PQ-10) [low P, high R^2 (Rsqr) values, and reasonable agreement between actual and predicted values]. The models are illustrated in Figures 4–7. Figure 4 shows the prediction profiler for silicone deposition of cationic cassia polymers (CC3.0, CC2.3, and CC1.9). As previously mentioned, the prediction profiler represents the predicted response as the variables are changed. These profilers show variables that significantly impact the behavior of the response. The dotted lines on the prediction profiler represent 95% confidence intervals of the predicted values. Figure 4 shows that the amount of surfactant and the micelle charge are statistically significant factors in the silicone deposition efficiency of cationic cassia polymers. By increasing the surfactant amount from 0.02 to 0.07 mol, the silicone deposition peak intensity decreases from ca. 25 to 5 kcps. Also, by increasing the micelle charge from 0.5 to 0.9, the silicone peak intensity increases from ca. 5 to 25 kcps.

The results show that the silicone deposition of the cationic cassia polymers decreases with increasing surfactant amount and increases with increasing micelle charge. Ionic strength does not have a statistically significant effect on the silicone deposition of cationic cassia

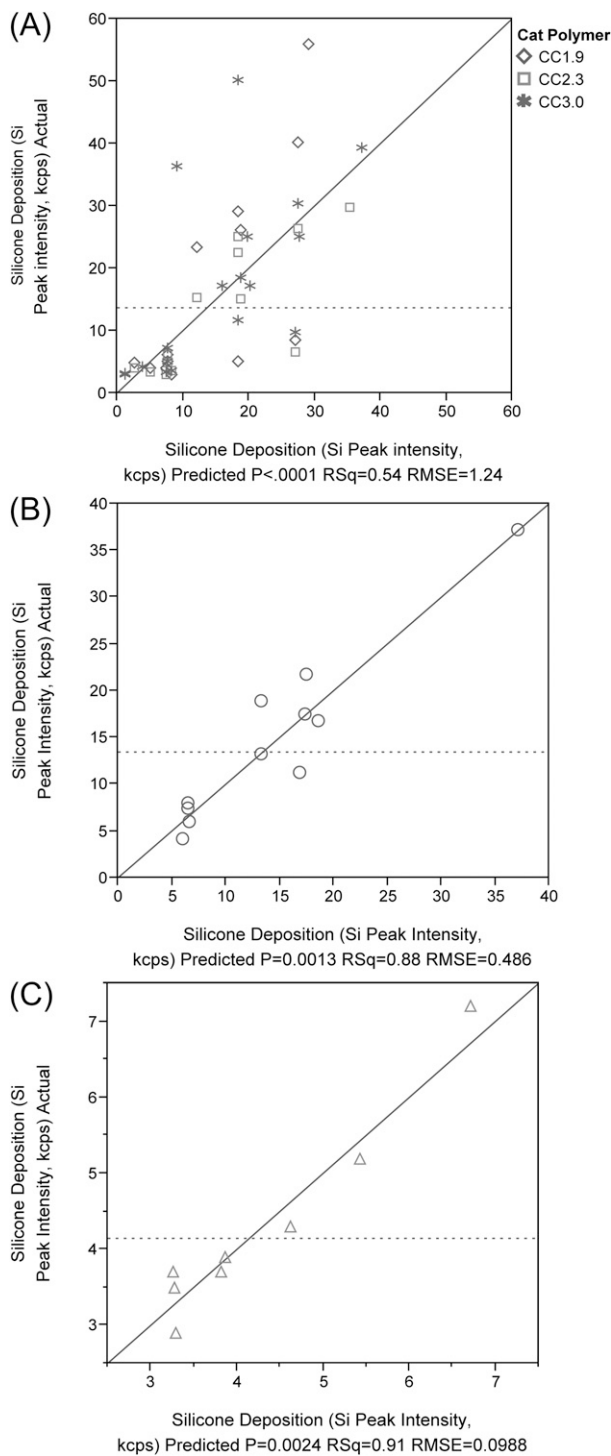


Figure 3. Model predictions for silicone deposition for cationic polymers: (A) cationic cassia polymers CC1.0, CC2.3, and CC3.0; (B) cationic guar CG0.98; and (C) cationic hydroxyethyl cellulose PQ-10 1.03.

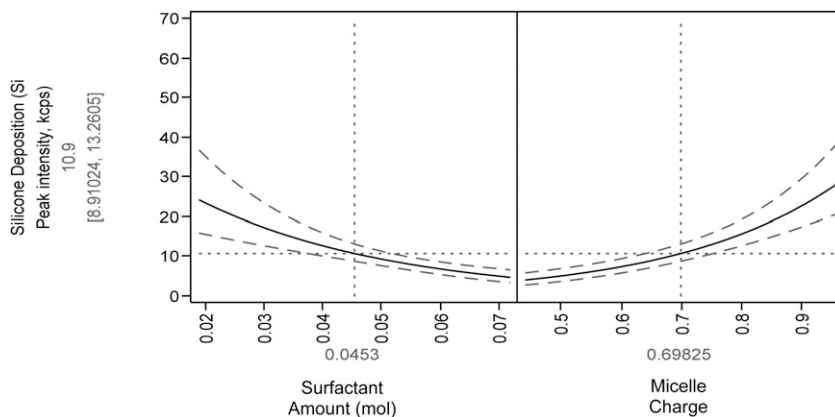


Figure 4. Prediction profiler for silicone deposition of cationic cassia polymers (CC3.0, CC2.3, and CC1.9).

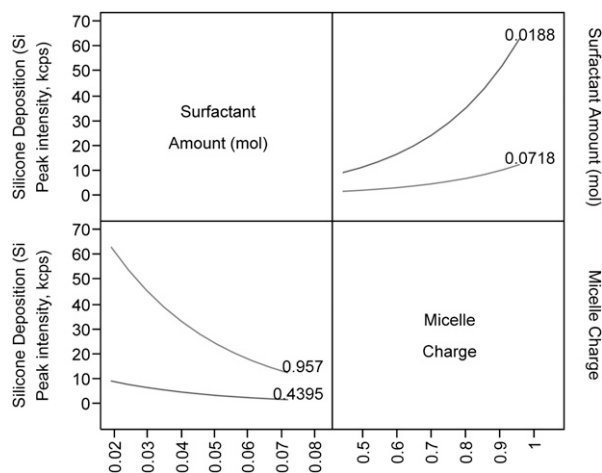


Figure 5. Interaction profiles for silicone deposition of cationic cassia polymers (CC3.0, CC2.3, and CC1.9).

polymers. In addition, there is a statistically significant interaction between the surfactant amount and the micelle charge. Specifically, in the lower left quadrant of Figure 5, the surfactant amount is on the x axis and the silicone deposition is on the y axis. The two curves represent different levels of micelle charge (0.4395 and 0.957, respectively, as indicated in the figure). One curve shows that when the micelle charge is low (i.e., 0.4395), increasing the surfactant amount from 0.02 to 0.07 mol yields a slight decrease in the silicone deposition peak intensity (from 10 to 5 kcps). When the micelle charge is high (0.957), increasing the surfactant amount from 0.02 to 0.07 mol yields a dramatic decrease in the silicone deposition peak intensity (from 60 to 20 kcps). That is, a greater decrease in the silicone deposition with increasing surfactant amount is obtained at high micelle charge. The same interaction is illustrated in the upper right quadrant of Figure 5. In this case, the micelle charge is on the x axis and the silicone deposition on the y axis. The two curves represent two levels of surfactant amounts (0.0188 and 0.0718 mol, respectively). When the total amount of surfactant is low (0.0188 mol), as the micelle charge is increased from 0.5 to 1,

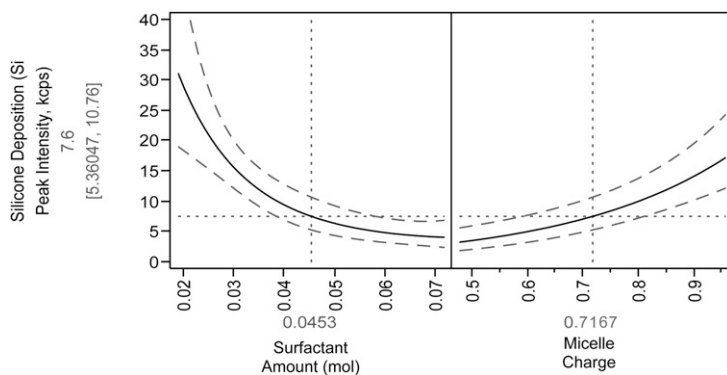


Figure 6. Prediction profiler for silicone deposition of cationic guar CG0.98.

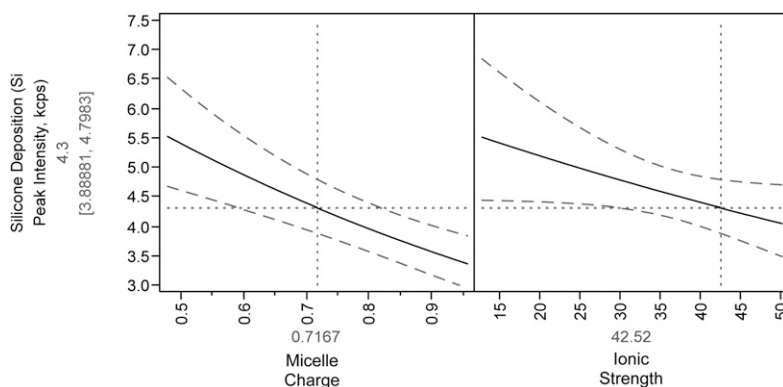


Figure 7. Prediction profiler for silicone deposition of cationic hydroxyethyl cellulose (PQ-10 1.03).

the silicone deposition peak intensity increases dramatically (from 10 to 60 kcps). When the total amount of surfactant is high (0.0718 mol), as the micelle charge is increased from 0.5 to 1, the silicone deposition peak intensity only increases slightly (from 5 to 10 kcps). A higher increase of silicone deposition with increasing micelle charge is obtained at lower surfactant amount, as seen in Figure 5. Such joint behavior between two or more variables on the response is called an interaction effect. Similar interpretation can be made from the predicted results illustrated in Figures 6–13.

Figure 6 shows the prediction profiler for silicone deposition of cationic guar CG0.98. The results show that, as seen for the cationic cassia polymers, the silicone deposition of cationic guar CG0.98 decreases with increasing surfactant amount and increases with increasing micelle charge. The effect of ionic strength is also not statistically significant on the silicone deposition for cationic guar. No statistically significant interactions between ionic strength, surfactant amount, and micelle charge were obtained for cationic guar CG0.98.

The prediction profiler for the silicone deposition of PQ-10 1.03 is shown in Figure 7. The results are very different from cationic cassia and cationic guar silicone deposition. The silicone deposition of PQ-10 1.03 decreases with increasing micelle charge and increasing

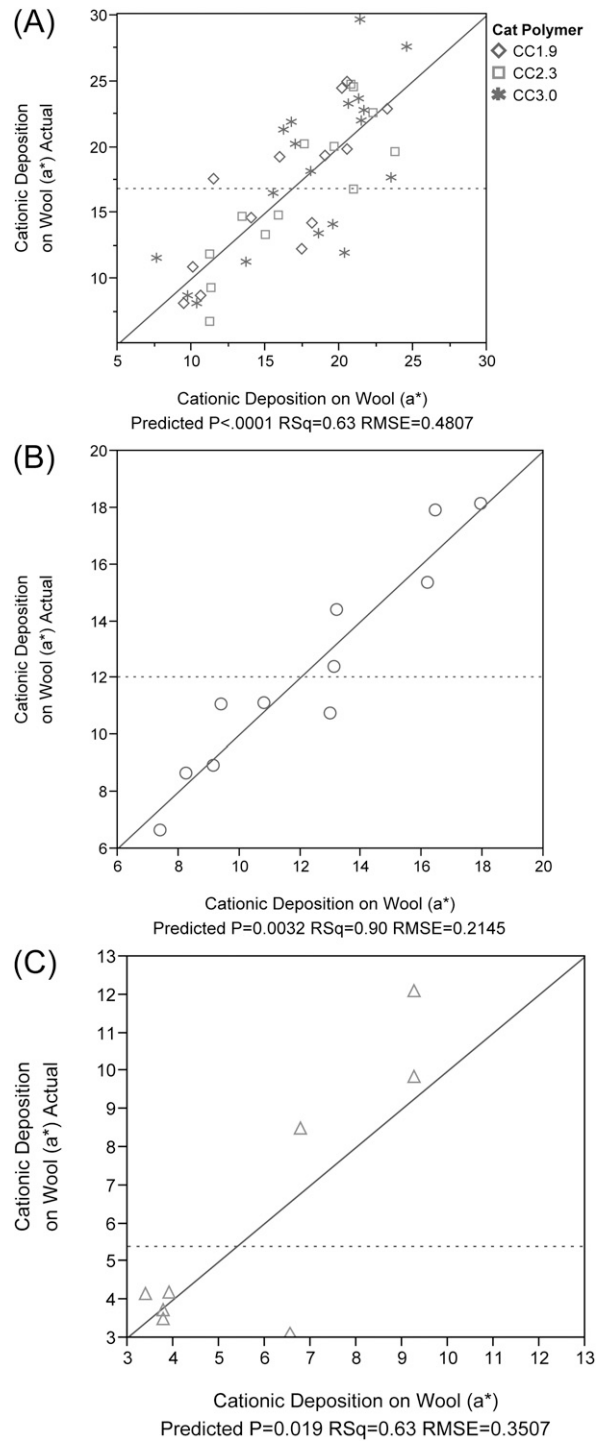


Figure 8. Model predictions for cationic polymer deposition: (A) cationic cassia polymers CC1.0, CC2.3, and CC3.0; (B) cationic guar CG0.98; and (C) cationic hydroxyethyl cellulose PQ-10 1.03.

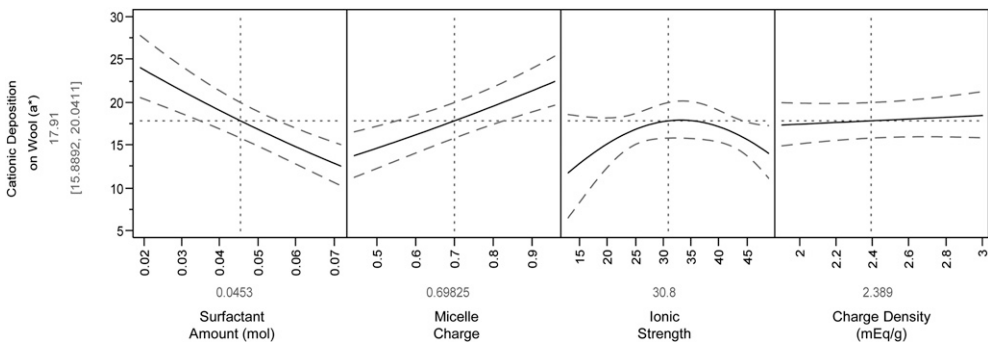


Figure 9. Prediction profiler for cationic cassia polymer deposition (CC3.0, CC2.3, and CC1.9).

ionic strength. The total amount of surfactant does not have a statistically significant influence on the silicone deposition of cationic hydroxyethyl cellulose. No statistically significant interactions between ionic strength, surfactant amount, and micelle charge were identified by the model.

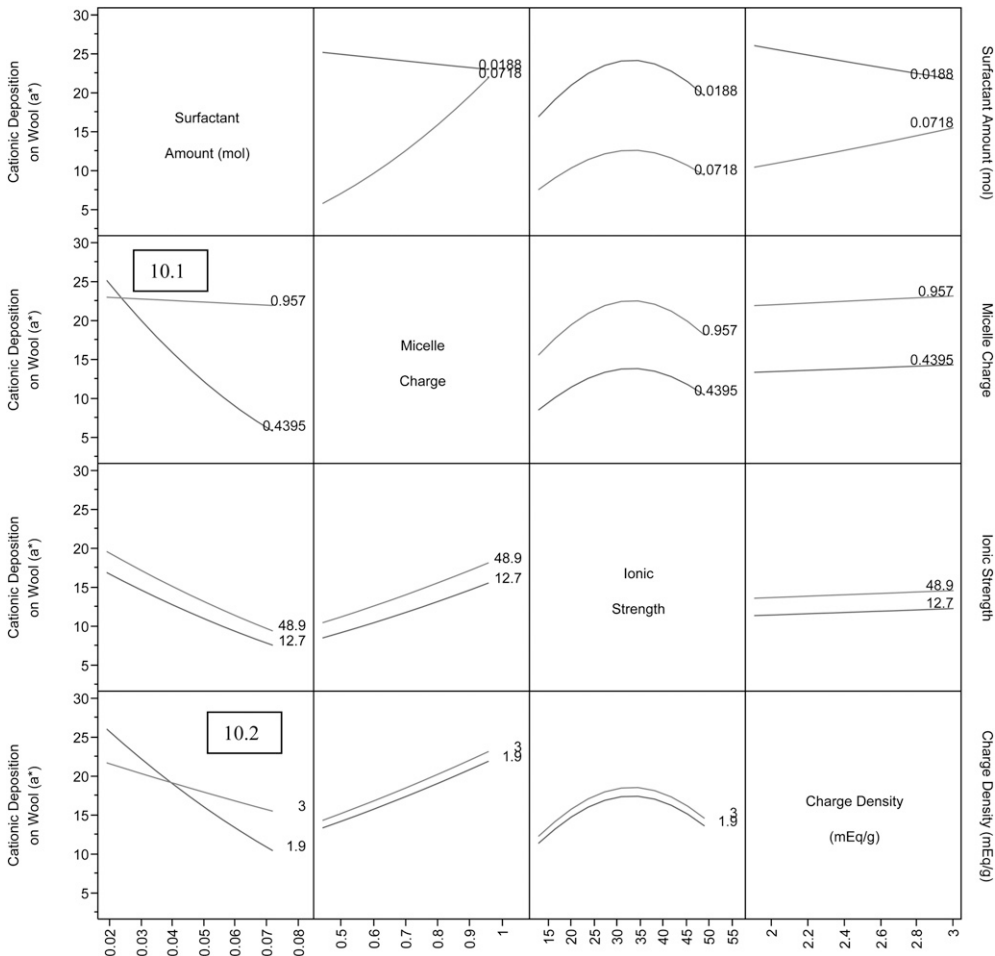


Figure 10. Interaction profiles for cationic cassia polymer deposition (CC3.0, CC2.3, and CC1.9).

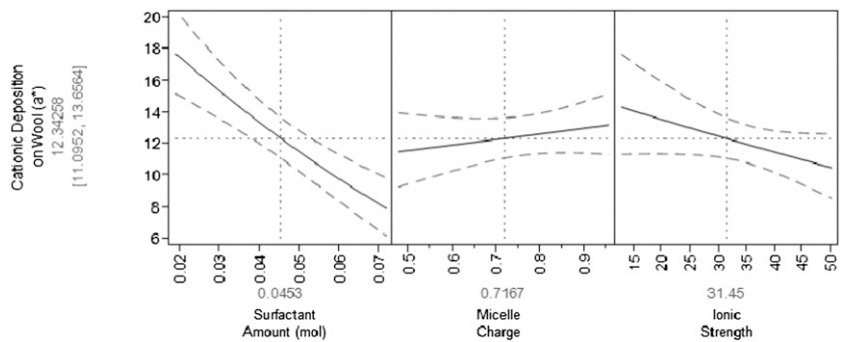


Figure 11. Prediction profiler for cationic guar polymer deposition (CG0.98).

CATIONIC POLYMER DEPOSITION

Statistical models for cationic polymer deposition were developed for each cationic polymer. Actual versus predicted cationic polymer deposition values are compared in Figure 8. Overall, relatively good models were obtained for all cationic polymers [low P , high R^2].

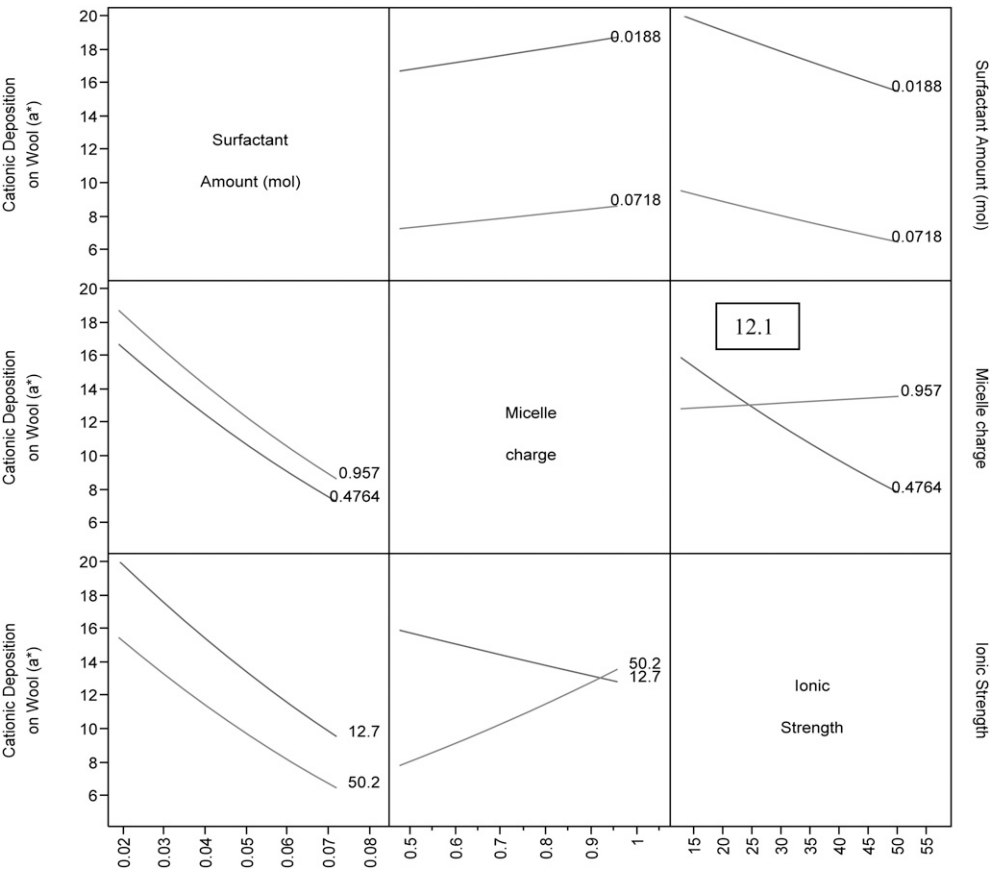


Figure 12. Interaction profile for cationic guar polymer deposition (CG0.98).

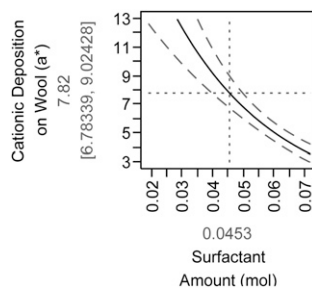


Figure 13. Prediction profiler for cationic hydroxyethyl cellulose polymer deposition (PQ-10 1.03).

(R_{sq}) values, and reasonable agreement between actual and predicted values]. The models are illustrated in Figures 9–13.

Figure 9 shows the prediction profiler for cationic cassia polymers deposition (CC3.0, CC2.3, and CC1.9). The results show that the cationic cassia polymer deposition decreases with increasing surfactant amount, increases with increasing micelle charge, and increases up to a maximum level with increasing ionic strength. Interactions between surfactant amount and micelle charge and between surfactant amount and cationic charge density are apparent (Figure 10). The cationic cassia polymer deposition decreases significantly with increasing surfactant amount at low micelle charge and only decreases slightly with increasing surfactant amount at high micelle charge. This interaction is shown in the panel labeled 10.1 in Figure 10. In addition, the cationic cassia polymer deposition decreases with increasing surfactant amount for the low charge density cationic cassia polymer and decreases slightly with increasing surfactant amount for the high charge density cationic cassia polymer, as seen in panel 10.2 in Figure 10.

Figure 11 shows the prediction profiler for cationic guar CG0.98 deposition. The results differ from the trends observed for cationic cassia polymers. For cationic guar CG0.98, polymer deposition decreases with increasing surfactant amount, slightly increases with increasing micelle charge, and decreases with increasing ionic strength. Also, a strong interaction between micelle charge and ionic strength is observed as seen in Figure 12. At high micelle charge, an increase in the ionic strength does not affect the cationic guar deposition. But at low micelle charge, an increase in the ionic strength leads to a significant decrease in cationic guar deposition (see panel 12.1).

The prediction profiler for PQ-10 1.03 polymer deposition is shown in Figure 13. The results are very different from those obtained for cationic cassia and cationic guar polymer deposition. For PQ-10 1.03, polymer deposition only decreases with increasing surfactant amount. Neither micelle charge nor ionic strength was observed to have a significant influence on PQ-10 1.03 polymer cationic deposition. No interactions between micelle charge, surfactant amount, and ionic strength were statistically significant.

The results clearly show that the molecular interaction between cationic polymer and anionic surfactant micelles is crucial for providing efficient silicone and cationic polymer deposition. In all cases, an increase in the amount of surfactant leads to a decrease in silicone or cationic polymer deposition. Higher amounts of surfactant lead to highly structured micelles or micelle with high aspect ratio, such as rodlike or lamellar structure. It is also possible that there is a different interaction (or conformation) between cationic

polymers with a high molecular weight or high rigidity, such as polygalactomannans, with micelles that have high aspect ratios (occurring at higher surfactant amount) compared to those with low aspect ratios (occurring at lower surfactant amount). The surfactant micelle–cationic polymer interactions are further influenced by the charge density on the micelle and that of the cationic polymer. For instance, the interaction of high charge density micelles with high cationic charge density polymers such as the cationic cassia polymers in this study, which typically have higher cationic charge densities than other commonly used cationic polymers, favors high silicone and cationic deposition. Several explanations are possible. The complex may be more likely to adhere to the negatively charged hair surface. Flocculation of the silicone droplets may be more efficient between cationic cassia polymers and highly negatively charged micelles. It is also possible that there is a different interaction (or conformation) between cationic cassia and micelles with high anionic charge compared to those with low anionic content, depending of the cationic polymer charge density.

The effect of ionic strength leads to a decrease in the silicone or cationic polymer deposition especially for the low cationic charge density polymers such as cationic guar CG0.98 or PQ-10 1.03. This can be explained by the work done by Dubin and Oteri (15). Specifically, these investigators showed that salt (or ionic strength) has a significant effect on both coacervation and precipitation of polyelectrolytes and oppositely charged micelles due to screening of the interaction between the two components. They suggest that both forms of aggregation can be suppressed or enhanced by addition of salt (see Figure 14). Screening of electrostatic interactions between polyelectrolytes and micelles by salt means that the binding affinity of micelles to polyelectrolytes increases with a decrease in salt concentration or decreasing ionic strength (i.e., in the initial formulation or also by shampoo dilution). As the binding affinity increases, the system can change from one in which no micelles are bound (phase I), to a positively charged complex with few bound micelles (phase II), then to a system with sufficient micelles for net neutrality (phase III), and finally to a negatively charged complex with excess bound micelles (phase IV). Similarly, the addition of salt can move the system from phase IV to phase I. Therefore, the complex [or coacervate (phase III)] can be “suppressed” or “enhanced” through changing the number

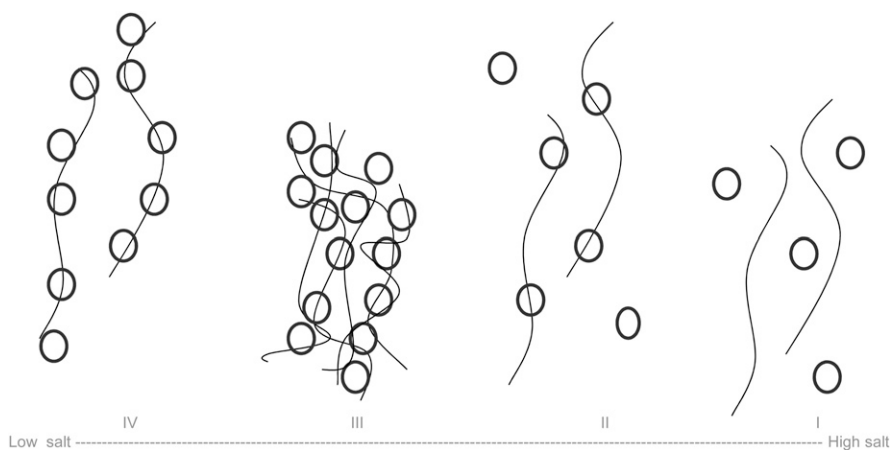


Figure 14. Effect of salt addition on micelle–polyelectrolyte interactions (14).

Table III
Summary of the Factors Influencing Silicone Deposition for Each Cationic Polymer (Increasing Factors)

Silicone deposition	Cationic cassia	Cationic guar	Cationic hydroxyethyl cellulose
Surfactant amount	↓ ^a	↓	
Micelle charge	↑	↑	↓
Ionic strength			↓
Cationic charge			

^aSignificant interaction with micelle charge (Figure 5).

of bound micelles. Thus, different coacervation and/or precipitation can be obtained from a surfactant/polymer system by changes in ionic strength or salt content. The data from this study show that the salt screening effect may influence the coacervation behavior and therefore the cationic and silicone deposition of the lower cationic charge density polymers such as cationic guar CG0.98 and PQ-10 1.03, compared to the cationic cassia polymers with higher cationic charge density.

CONCLUSIONS

The results show that different factors influence the conditioning performance of different cationic polymers. The formulation composition has a strong influence on the silicone and cationic polymer deposition that are primary determinants of the conditioning performance. Three parameters are highlighted to be of importance in determining silicone and cationic polymer deposition: ionic strength, average surfactant charge (micelle charge), and the total amount of surfactant. Silicone and cationic polymer deposition results can be predicted to a high confidence level using models that incorporate these three factors. There appears to be several mechanisms that are of importance in determining silicone and cationic deposition and, therefore, conditioning performance. Which of these factors is operative may depend on the cationic polymer molecular weight, cationic charge density, polymer chain flexibility, and solubility. A summary of these factors for silicone deposition and cationic polymer deposition is in Tables III and IV, respectively. Silicone and cationic deposition data indicate that increasing the interaction between the cationic polymer and surfactant by either using a more highly charged cationic polymer, decreasing the aspect ratio of the surfactant structuring (lower surfactant amount), or decreasing the ionic strength (less ionic interaction shielding) may contribute to better deposition.

Table IV
Summary of the Factors Influencing Polymer Deposition for Each Cationic Polymer (Increasing Factors)

Cationic deposition	Cationic cassia	Cationic guar	Cationic hydroxyethyl cellulose
Surfactant amount	↓ ^a	↓	↓
Micelle charge	↑	↑ ^b	
Ionic strength	↑	↓	
Cationic charge	↑		

^aSignificant interactions with micelle charge and cationic charge (Figure 10).

^bSignificant interaction with ionic strength (Figure 12).

This is likely to be the result of better adhesion of the polymer–surfactant complex to the hair and/or higher efficiency to flocculate the silicone or cationic polymer.

ACKNOWLEDGMENTS

The authors thank Lubrizol Advanced Materials (a wholly owned subsidiary of The Lubrizol Corporation) for permission to publish and John Mullay, Denise Wade Rafferty, and Daniel Hasman for their useful discussion of this work.

REFERENCES

- (1) R. Y. Lochhead, Conditioning shampoo, *Soap Cosmet. Chem. Spec.*, **68**, 10, 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 Interf. 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 Interf. 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. Toilet. Manufact. Worldwide*, 1–4 (2003).
- (7) C. Lepilleur, J. Mullay, C. Kyer, P. McCalister, and T. Clifford, Use of statistical modeling to predict the effect of formulation composition on coacervation, silicone deposition, and conditioning sensory performance of cationic cassia polymers, *J. Cosmet. Sci.*, **62**, 161–177 (2011).
- (8) S. Chiron, Performance and sensory benefits of cationic guar in hair care applications, *Cosmet. Toiletries*, **119**, 2, 47–51 (2004).
- (9) M. Gamez-Garcia, Polycation substantivity to hair, *IFSCC*, **4**, 2, 99–107, (2001).
- (10) F. Utz *et al.*, Cationic cassia derivatives and applications therefore, *US Patent 7,262,157 B2* (2007).
- (11) 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).
- (12) 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).
- (13) 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 Surface B*, **19**, 127–135 (2000).
- (14) J. Sall and A. Lehman, *JMP Start Statistics: A Guide to Statistics and Data Analysis Using JMP and JMP IN Software*. (Duxbury Press, SAS Institute, Cary, NC, 1996), pp. 340.
- (15) Y. Wang, K. Kimura, Q. Huang, and P. L. Dubin, Effects of salt on polyelectrolyte–micelle coacervation, *Macromolecules*, **32**, 7128–7134 (1999).

