

Chapter 2

Effect of Hydrophobic Substitution on Cationic Conditioning Polymers

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Cationic cellulosic polymers are formulated with anionic surfactants in shampoos and body washes as conditioners and deposition aids. During dilution, the polymer and surfactant undergo a series of association and microstructure changes: from a condensed network to globular aggregation to inter-chain association with micelles. Cationic polymer structure impacts the polymer/surfactant interaction. The addition of hydrophobic chains on the polymers significantly changes deposition and conditioning properties. In general, deposition of benefit agents from shampoos and body washes increases in the presence of these modified polymers. Conditioning in clear formulations also improves. These performance changes depend on the absolute molar substitution of the hydrophobic moiety as well as the surfactant system. The presence of even very low levels of hydrophobe alters interfacial reactivity with surfactants and surfaces influencing both coacervate formation and deposition.

Polyquaternium-10 (PQ-10) is the INCI name for cationic (trimethyl ammonium) hydroxyl ethyl cellulose (HEC) polymers that are used in shampoo systems to impart conditioning properties to hair including good feel properties and manageability. More recently, these polymers are used in body wash formulations to improve skin feel during washing and after drying and improved deposition of oils. Nomenclature for commercial PQ10 polymers reflects the relative molecular weight and charge density. The first two letters represent charge density (JR:~1.7% nitrogen, LR: ~1.0% Nitrogen). The following numbers/letters indicate relative molecular weight (400:medium, 30M:-high).

In shampoo and body wash formulations, the cationic polymer and surfactant exist together in a single phase. Upon dilution during washing and rinsing, cationic HEC polymers form a complex with the surfactant system that phase separates from the bulk solution. This phase separation (or coacervation) is a well-known phenomenon known as the "Lochhead Effect" (1-3). The coacervate is a gel like phase that contains a high level of cationic polymer that deposits on negatively charged substrates, forming a clear film. The haze formed by coacervate formation is readily measured. In addition, coacervates aid in the deposition of insoluble actives, such as silicone (4,5). Deposition efficiency is dependent on polymer molecular weight as well as cationic charge density. Recent work by Zhou, et al. (6) investigates molecular weight effects and ethylene oxide chain length on the phase behavior of cationic hydroxyethyl cellulose at different concentrations of sodium dodecyl sulfate (SDS). These phase changes include a condensed network, globular aggregation (coacervation) and inter-chain association with micelles (Figure 1).

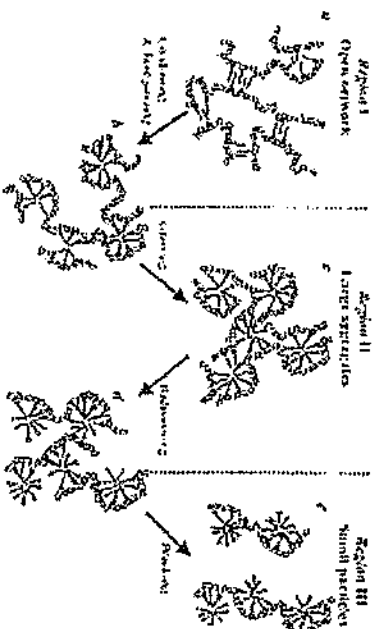


Figure 1. Structural models of cationic HEC-SDS complex at each phase evolution stage. (Reproduced from reference 6. Copyright 2004 American Chemical Society.)

Zhou, et al. show at low surfactant, the polymer is soluble with a hydrodynamic radius (Rh) about 100 nm near the phase boundary. As surfactant concentration increases, Rh increases and phase separation occurs. As the surfactant boundary is approached, particle size is maximized. Addition of surfactant to concentrations above the upper phase boundary indicates resolubilization of the polymer and decreased Rh. The complex microstructure relationships between polymer and surfactants predict additional functional and performance effects upon the addition of hydrophobic chains onto the polymer backbone (Figure 2).

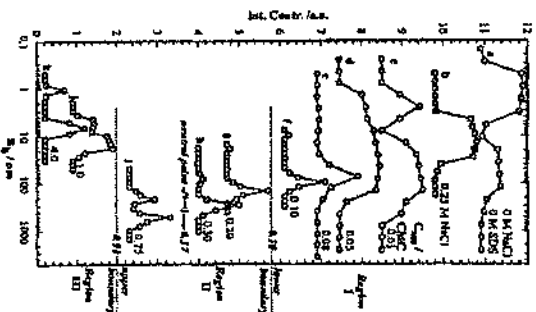


Figure 2. Apparent hydrodynamic radius (Rh) distribution of 0.2 wt % EO22MW110 solution in 0.25 M NaCl (b) and in differently concentrated SDS solution (c-k). (Reproduced from reference 6, Copyright 2004 American Chemical Society.)

Materials and Methods

All materials were used as received.

Cationic polymers: PQ10 and PQ67 from Amerchol Corporation
Surfactants (Cognis): Standapol ES-2 (sodium laureth sulfate, SLES-2),

Velvetex BK-35 (cocamidopropyl betaine, CAPB), Velvetex CDC (disodium cocamphodiacetate, DSCADA)

Silicone: Dow Corning 2-1664 emulsion

Hair: International Hair Importers and Products

Vitro-Skin® IMS Inc.

Wet combing: Wet combing is measured using a Dia-Stron Miniature Tensile Tester. The force required to pull a comb through a wet hair tress treated with surfactant alone and then surfactant plus polymer is measured. Five grams of hair is washed with 0.5 grams of a shampoo, and rinsed at constant temperature. The difference in force required to comb the hair tress is wet comb reduction.

Coacervate study: Haze measurements were performed using a nephelometer or a Nippon Denshoku 300A hazemeter 2 minutes after diluting formulation 2.5 to 20 times with water and mixing at room temperature.

Silicone deposition: The amount of silicone deposited on hair after shampooing was measured. Five grams of hair was washed with 0.5 grams of a shampoo, and rinsed at constant temperature. Hair was extracted with a 1:1 mixture of methyl butyl ketone and toluene. Atomic absorption spectroscopy was used to measure silicone content; reporting µg silicone/g hair.

Sunflower seed oil deposition: A 3-6 cm piece of Vitro-skin® was washed with 0.15 mL body wash and rinsed at constant temperature. Dried skin was extracted with heptane and analyzed for SSO using gas chromatography.

Results and Discussion

The effect of molecular weight and charge density of cationic HEC polymers (Polyquaternium 10 or PQ10) on silicone (0.5 µ dimethicone) deposition from a simple shampoo formulation (15.5% SLES-2 / 2.6% DSCADA, 0.25% polymer, 1% silicone) is shown in Figure 3. Both parameters affect the overall performance of the polymers in depositing silicone. This data is consistent with coacervate formation as a function of dilution level.

The haziness of the diluted solution was monitored as an indicator of coacervate formation and was measured with a Nephelometer 2 minutes after dilution. In this case, the coacervate peak-height increases with molecular weight, suggesting more coacervate leads to increased deposition and may simply be a function of the increased ability of the larger polymer to flocculate the insoluble silicone onto the hair rather than a change in interactions in solution. Coacervate peaks shift significantly (from 5 to 10 fold dilution), however, as the charge density decreases (Figure 4). This shift is independent of surfactant base (Shampoo 1: 15.5% sodium laureth sulfate (SLES-2) / 2.6% cocamidopropyl betaine (CAPB), Shampoo 2: 15.5% SLES-2 / 2.6% disodium cocamphodiacetate (DSCADA) Data not shown). Differences in silicone deposition coupled with coacervate peak shifts at varying charge density suggest

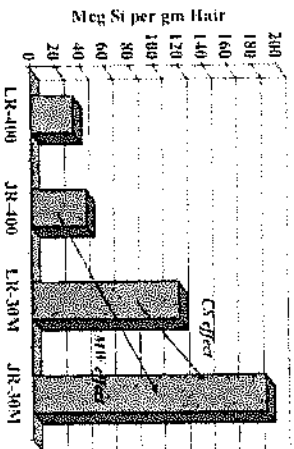


Figure 3. Silicone deposition onto European brown hair using PQ10. Low molecular weight polymers: -400, high molecular weight polymers: -30M; low charge density: LR, high charge density: JR. (15.5% SLES-2 / 2.6% DSCADA, 0.25% polymer, 1% silicone)

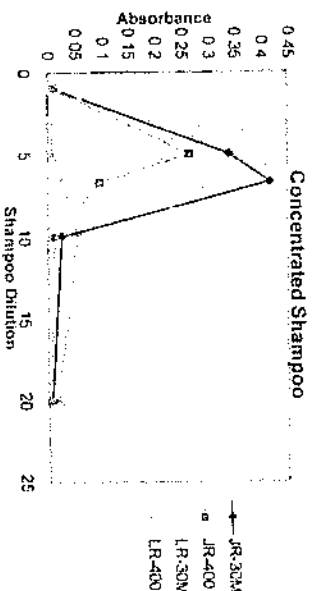


Figure 4. Coacervate haze curves of PQ10 polymers measured using a Nephelometer. Low molecular weight polymers: -400, high molecular weight polymers: -30M; low charge density: LR, high charge density: JR. (15.5% SLES-2 / 2.6%CAPB, 0.5% polymer) (See page 1 of color inserts.)

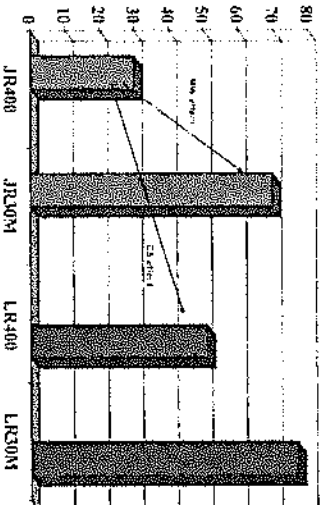


Figure 5. Wet combing reduction of single bleached hair washed with shampoo containing PQ10 polymers. Low molecular weight polymers: -400, high molecular weight polymers: -30M; low charge density: LR, high charge density: JR. (15.5% SLES-2 / 2.6% DSCADA, 0.5% polymer)

Based on the data in Figures 3-5, both silicone deposition and conditioning are favored by higher molecular weight polymers, regardless of charge substitution. Interestingly, early peak dilution (higher charge) favors silicone deposition while late peak dilution and wide coacervation zone (lower charge) favor conditioning. PQ10 also effects sunflower seed oil (SSO) deposition from body wash formulations. Similar to shampoo systems, increased molecular weight and charge density result in increased SSO deposition onto skin (data not shown).

According to Zhou, et al (6) differences in polymer surfactant microstructures on dilution are apparent with cationic HEC polymers containing lower levels of ethylene oxide (EO) substitution from typical PQ10. Less EO suggests the polymer will be less hydrophilic and have more hydrophobic

the interaction of the polymer with surfactant is highly dependent on charge density. Wet combing studies are used to measure relative conditioning of the hair. The force required to pull a comb through wet hair is measured with a Diasiron and compared to a control. The more wet comb force reduction, the better the conditioning. Polymer dependence on conditioning effects, as measured by wet combing, show that as molecular weight increases, wet combing increases. In contrast, while charge increases, wet combing decreases. The effect of molecular weight, however, appears to partially compensate for the effect of charge on overall wet combing (Figure 5).

character. The change in microstructure observed with low EO polymers suggests increased hydrophobicity of cationic HEC will affect interaction with surfactants and hence polymer performance. Zhou, et al. determined polymers with low EO substitution have a broadened concave zone (suggesting better wet combing) and increased Rh (suggesting better deposition). As was shown in Figure 2, the largest Rh occurs at high surfactant concentration (low dilution). Since lower peak dilution corresponds to better deposition (Figures 3 & 4), it is possible a more hydrophobic polymer can both increase peak area (maximize wet comb) and maintain maximum peak dilution at low dilution levels (maximize deposition).

In order to understand the effect of hydrophobicity on cationic HEC, a new polymer family, Polyquaternium 67 (PQ 67), was developed. PQ 67 is a high viscosity quaternized hydroxyethyl cellulose (HEC) polymer with cationic substitution of trimethyl ammonium and dimethyldodecyl ammonium (Figure 6). For experiments in shampoo systems, cationic substitution was fixed at ~ 0.2, which corresponds to a weight-percent nitrogen of ~1.0%, while substitution of hydrophobic dimethyldodecyl ammonium is held at hydrophobic substitution < 0.01. Four hydrophobic levels were tested with designations SL-5, SL-30, SL-60, and SL-100, where the molar substitution of relative hydrophobe increases with increasing number from 5 to 100. The results indicate the addition of even low concentrations of hydrophobe leads to significant differences in performance.

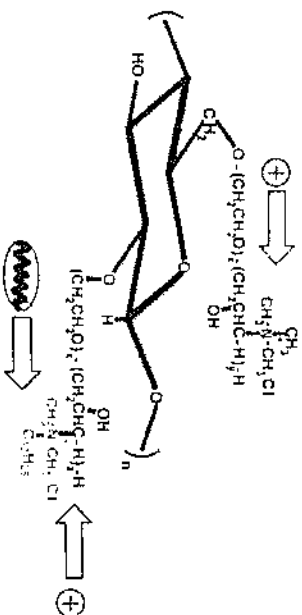


Figure 6. Polyquaternium 67: cationic HEC containing Hydrophobic substitution < 0.01 dimethyldodecyl ammonium.

A significant increase in wet combing performance is seen in shampoos formulated with hydrophobically modified polymers. This performance

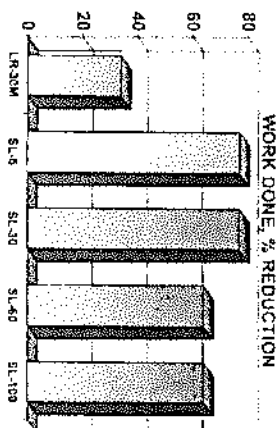


Figure 7. Wet combing force reduction of single bleached European brown hair using hydrophobically modified cationic HEC polymers. 15.2% SLES-2/2.56% DSCADA/0.3% polymer.

enhancement does not continue to increase with higher levels of hydrophobic substitution (SL-60 and SL-100) suggesting performance differences are not due to molecular weight effects, but to the hydrophobe itself. (Figure 7)

Silicone deposition onto hair is shown in Figure 8. Similar to wet combing data, silicone deposition increases in the presence on hydrophobe. Given the low level of hydrophobe, there is not a significant increase in molecular weight of these polymers. The near doubling of silicone deposition cannot be explained by simple increased flocculation and bridging caused by a larger polymer. It is more likely the hydrophobe is changing the interaction of the polymer with the surfactant and polymer with silicone.

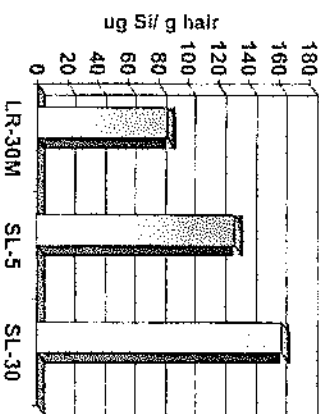


Figure 8. Silicone deposition on European brown hair of hydrophobically modified cationic HEC polymers. 15.2% SLES-2/2.56% DSCADA/0.3% polymer/0.25% polymer/1% dimethicone blend.

PQ67 polymers were also investigated in body wash systems (11% SLES-2, 4% CAPB, 15% sunflower seed oil, and 0.5% polymer). These polymers use the designation SK. The SK polymers tested vary charge substitution rather than hydrophobic density level (Figure 9). The effect of molecular weight on deposition of sunflower seed oil onto *Vitro*-skin is shown in Figure 10 using commercial PQ10 polymers. As with silicone deposition on hair, higher molecular weight polymer of either low or high charge density (LR and JR polymers, respectively) exhibits higher sunflower seed oil deposition. This increase in deposition may be related to large polymer bridging effects. Figure 10 also shows the effect of charge substitution on deposition. The higher charged JR30M (~1.7% N) deposits more oil than the lower charged LR30M (~1.0% N).

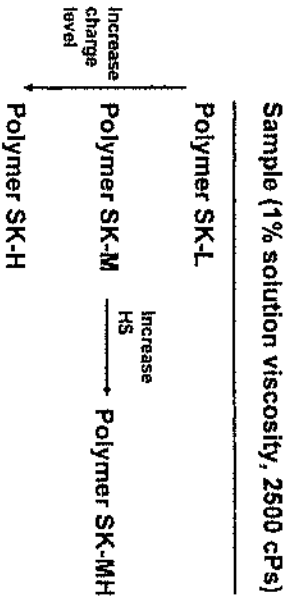


Figure 9. SK polymers used in body wash formulations. Hydrophobe density for SK-L, SK-M, & SK-H similar to SL-5; SK-MH similar to SL-30.

Additional charge substitution effects for SSO deposition are shown in Figure 11. In the presence of hydrophobe, rather than simply increasing with increasing charge, deposition actually peaks between LR30M (1.0% N) and JR30M (1.7% N).

As predicted from the low EO substitution studies and the results above, the presence of hydrophobe shifts coacervate curves significantly (Figure 12). The peak coacervate formed with SK-M (1.25% nitrogen) corresponds to peak coacervate formed with JR30M (1.75% nitrogen). The addition of hydrophobe shifted the peak coacervate to early dilution, leading to increased deposition. A similar peak shift is seen with SK-L (1.05% nitrogen) compared with essentially the same nitrogen level of LR-30M (0.95% nitrogen). The only difference being the presence of hydrophobe on SK-L. Both SK polymers show significantly broader coacervate curves, therefore accounting for the improved wet combing as well. This non linear effect of charge and hydrophobe substitution suggests

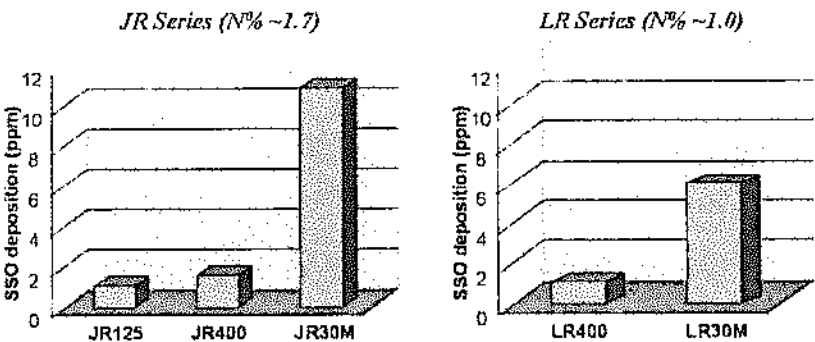


Figure 10. Molecular weight effects of sunflower seed oil deposition on Vitro skin: 11% SLES-2, 4% CAPB, 15% sunflower seed oil, 0.5% polymer. (MW: 125<400<30M. Charge: LR~1.0%, JR ~1.7%)

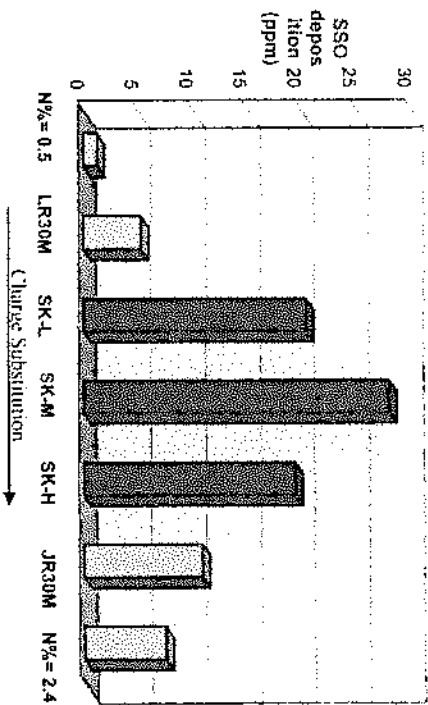


Figure 11. Effect of charge density in the presence of hydrophobe on surfloer seed oil deposition on in Viro skin. 11% SLES-2, 4% CAPB, 15% sunflower seed oil, 0.5% polymer (SK-L, 1.05%N; SK-M, 1.25%N; SK-H, 1.45% N)

specific structure/function relationships on the interaction of the polymer and surfactant which influence overall formulation performance.

Conclusion

The cationic HEC polymer architecture was found to have a significant effect on the formation and dissolution of surfactant-polymer coacervates, which were shown to be critical in deposition of water insoluble actives from shampoos and body wash formulations. A new compositional variant of cationic HEC polymers was synthesized by adding low levels of hydrophobic substitution (dodecyl chain). These hydrophobic chains had a pronounced affect on the deposition of insoluble actives presumably by associating with the surfactants through hydrophobic interaction, altering the interactions, and affecting overall formulation performance. The coacervate curves shifted significantly to the left (lower dilution) while continuing over a broad zone. With the addition of low levels of hydrophobic substitution, significant improvement in coacervate formation, and silicone and sunflower seed oil deposition were achieved. The data also reveal that coacervate curves can be used to predict overall polymer performance in rinse off systems.

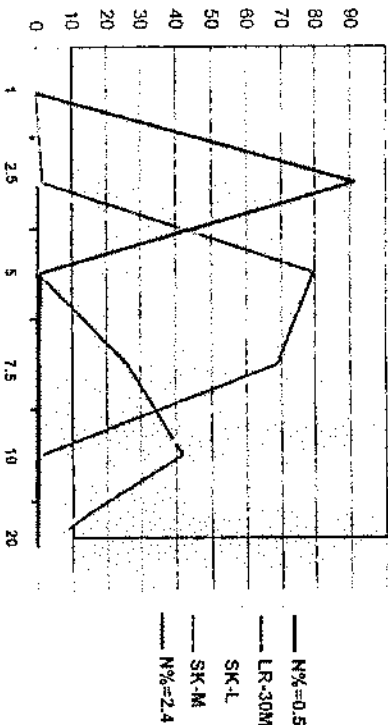


Figure 12. Coacervate haze curves at different charge density measured using a haze meter. 11% SLES-2, 4% CAPB, 0.5% polymer. (See page 1 of color inserts.)

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