Surface Wettability of Human Hair. III. Role of Surfactants in the Surface Deposition of Cationic Polymers.

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Synopsis

The effects of low molecular weight surfactants of different ionic characteristics on the deposition of a quaternized cellulosic polymer onto the surface of hair from solution have been studied. The uniformity of deposition and the substantivity of the deposited material has been assessed from measurements of the surface wettability of treated hair fibers with water. The results show that anionic surfactants at low-to-moderate concentrations bind with the cationic polymer so that the substantive layer deposited on the fiber surface tends to be hydrophobic due to orientation of lipid chains away from the surface. At high concentration, additional anionic surfactant molecules interact with the cationic polymer molecule by hydrophobic bonding, reducing the polymer–surfactant complex to an anionic polyelectrolyte which has little substantivity to the fiber surface. Cationic surfactants, on the other hand, do not interact with the polymer because of charge repulsion but compete with the polymer for negatively charged sorption sites on the surface, greatly reducing surface coverage by the polymer. The interaction of amphoteric surfactants with the polymer depends on the pH of the solution. Studies on experimental shampoos containing anionic and amphoteric surfactants confirmed these observations, and indicated, in addition, that dilution of the shampoo in the presence of hair plays a significant role in the deposition of the polymer on the hair surface.

INTRODUCTION

There are a number of hair care products which are formulated to deposit compounds on the surface of hair to enhance its aesthetic appearance and improve manageability. These formulations usually contain a low molecular weight anionic surfactant which acts as a cleansing agent and a cationic surfactant or a polymer which deposits on the cleaned fiber surface, changing its surface characteristics. The entire process results in significant changes in interfiber interactions and in improved assembly behavior.

Combinations of ionic surfactants and polymers in solution can lead to interactions which affect the adsorption characteristics of the molecular species. To understand the nature of these interactions and their implications for the adsorption of these substances on the hair fiber surface, the behavior of a cationic polymer (JR-400) in the presence of low molecular weight anionic, cationic, and amphoteric surfactants has been investigated.

Furthermore, these studies have been extended to experimental shampoo formulations containing a different cationic polymer in combination with two low molecular weight surfactants. Adsorption of polymer molecules from solution onto the surface of a solid depends on the relative interaction of the molecular segments with the surfactant and the solvent and on the phase equilibrium of the polymer–surfactant complex. The amount of polymer adsorbed from solution onto the surface of the solid can be increased by shifting the phase equilibrium in the appropriate direction. This can be

CCC 0021-8995/85/050937-17$04.00

achieved by diluting such solutions in the presence of the solid surface. In the case of a conditioning shampoo, dilution occurs when the shampoo is applied to wet hair. In order to understand the nature of this process, the effect of dilution on the extent of surface coverage has been investigated by measuring changes in surface wettability.

EXPERIMENTAL

These studies have been conducted on European dark brown hair cleaned by extraction with $CH_3OH/CHCl_3/CH_3OH$ in that order followed by exhaustive rinsing with distilled water. The following materials were used in this work: (1) Polymer JR-400 (Union Carbide Corporation); (2) Sodium lauryl sulfate (SLS); (3) Triton X-400 (TR-X-400) (Rohm & Haas Company); (4) Miranol C2MSF (MR-C2MSF) (Miranol Chemical Co.). Polymer JR-400 is a cationic polymer. The other three substances are surfactants of low molecular weight two of which have been discussed elsewhere.[1,2] Miranol C2MSF is an amphoteric surfactant whose structure will be discussed later.

The experimental shampoos used in this work were provided by Ciba-Geigy (Basel, Switzerland). The principal components of the shampoos were: shampoo II, 0.85% BINA4173, 14.30% Miranol C2MSF, 3.6% citric acid; shampoo IV, 0.85% BINA4173, 35.0% Texapon TH. Each shampoo contained minor amounts of other materials. The polymer BINA4173 is a cationic polymer, and Texapon TH is trialkanolamine lauryl sulfate, i.e., an anionic surfactant. Shampoos I and III contained no polymer BINA4173 but, otherwise, had the same formulation as Shampoos II and IV.

Solutions for treatment were prepared by dissolving the low molecular weight surfactant (SLS TR-X-400, or MR-C2MSF) in 100 mL of water, followed by addition of 1 g of polymer JR-400 under continuous stirring until a clear solution was obtained. In some cases a clear solution could not be obtained as a result of precipitation of the polymer–surfactant complex. Hair fiber snippets were treated with the polymer–surfactant solutions at 40°C for 0.9 ks, followed by air drying and conditioning overnight at 65% RH and 21°C prior to wetting force measurements.

In the case of experimental shampoos based on polymer BINA, fiber snippets were first kept in distilled water at 21°C for 1.8 ks (simulating wet hair) and then transferred to a solution of the shampoo at appropriate dilution for 0.9 ks at 40°C, followed by air drying and conditioning at 65% RH and 21°C.

The surface of the treated fibers was characterized via advancing wetting force curves obtained during immersion of about 3–4 mm lengths of the fiber into distilled water. This procedure was repeated on the same fiber in multiple immersions to study desorption and substantivity of the adsorbed material. The details of these procedures have been discussed in an earlier article.[1]

RESULTS AND DISCUSSION

SLS–JR-400

The properties of solutions containing 1% of polymer JR-400 and various amounts of SLS are included in Table I. Addition of small quantities of SLS increases the viscosity of the polymer solution significantly. At concentra-

TABLE I

Advancing Wettabilities of Hair Fibers Treated with 1% JR-400 Solution Containing Various Amounts of SLS (Multiple Immersions in Water)

Surf. concn (%)	γ (mN/m)		Nature of solution	Advancing wettability (mN/m)[a]			
	Surf.	Polymer + surf.		Untr.	Imm I	Imm II	Imm III
0	—	64.2	Clear, viscous	− 8.4± 3.6	57.7±14.9	16.0± 4.6	13.1± 4.8
0.001	53.8	44.7	Clear, viscous	−11.9± 4.7	73.2±13.0	− 5.0± 3.5	− 1.6±11.9
0.01	35.6	41.6	Clear, viscous	− 5.4±12.9	82.4± 3.5	− 1.5± 3.5	− 1.3± 6.6
0.1	28.9	41.4	Clear, viscous gel	1.3±10.6	87.6± 4.1	7.3± 5.4	−13.9± 5.5
0.2	32.9	39.8	Opalescent, viscous gel	−12.1± 4.3	78.9± 2.7	− 2.7± 3.7	−10.9± 2.4
1.0	35.5	35.3	Opalescent, precipitate	− 7.0±10.0	27.7± 7.9	−28.4±17.4	−36.4± 8.1
2.0	32.7	34.8	Clear, less viscous	−15.8± 1.9	40.5±15.5	−41.0± 8.3	−36.2±11.5
10.0	31.8	33.3	Clear, less viscous	0.9± 2.1	54.1± 5.9	− 1.5± 3.8	− 1.7± 4.8

[a] Each entry is an average of six measurements at the 95% confidence level.

tions above 0.1%, the solution begins to develop a gel-like structure; at ~0.2% the solution begins to develop opalescence, and at ~1% heavy precipitation occurs. Mixtures containing 2% and 10% SLS give clear, less viscous solutions after prolonged stirring.

These observations can be explained on the basis of interaction of anionic surfactant molecules with the cationic polyelectrolyte molecules of JR-400, shown schematically in Figure 1. The first step seems to be the formation of an electrovalent bond between lauryl sulfate anions and the cationic sites on the polymer [Fig. 1(a)], followed by hydrophobic bonding of lauryl chains (concentration range 0.1–~1%). This leads to a thixotropic gel structure, characterized by high viscosity which characteristically decreases when the solution is stirred because of the weak nature of the hydrophobic bonds. It should be noted that not all the charges on the polymer are associated with lauryl sulfate anions at this stage. Indeed, when the concentration of the surfactant is high enough to form a 1:1 complex, heavy precipitation occurs. Further addition of SLS causes the addition of a second layer of lauryl sulfate anions, once again, by hydrophobic bonding between the hydrocarbon chains [Fig. 1(b)], leading to the breaking up of the precipitate and to the formation of polyelectrolyte molecules with reversed charges. This explains the solubilization of the precipitate and the reduction in viscosity at higher concentrations of SLS.
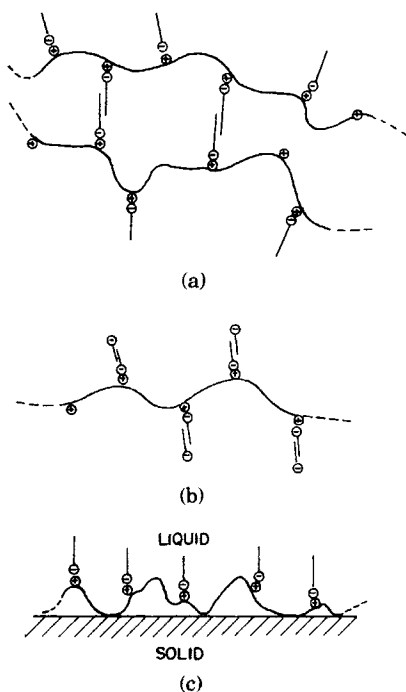

(a)

(b)

LIQUID

SOLID

(c)

Fig. 1. Proposed molecular interactions: (a,b) hydrophobic bond formation between lauryl chains associated with the cationic polymer; (c) adsorption of polymer–surfactant complex on the solid surface.

According to the data in Table I, maximum precipitation is observed at an SLS concentration of ~1%. Assuming the formation of a 1:1 complex and a molecular weight for JR-400 of ~400,000, the number of cationic sites on the JR-400 molecule is ~1390. This is close to the value of 1222 obtained from electrophoretic mobility measurements,[3] in which the formation of a neutral complex was observed at an SLS concentration of 0.088% for a 0.1% solution of JR-400.

The effect of SLS concentration on the surface tension of JR-400 solutions is shown in Figure 2. That the surface activity of polymer JR-400 itself is very low is shown by the high surface tension (~65 mN/m) of a 1% solution. Association of lauryl chains with the cationic molecules increases the surface activity of the complex,[3] which improves the spreading of these solutions on the surface of hair.

Wetting force curves are shown in Figure 3 (a)–(c) for fibers treated with 1% polymer JR-400 solutions and with JR-400 containing increasing concentrations of SLS. Statistical trends are shown in Table I. As discussed previously,[1] dip coating with a JR-400 solution by itself produces a discontinuous deposit on the fiber surface evidenced by the gross variations in the wetting force curve shown in Figure 3(a). This has been attributed to the disparity between the high surface tension of the treatment solution and the low critical surface tension of the essentially hydrophobic epicuticle of the hair fiber. Additions of small amounts of SLS to the JR-400 solution significantly lowers the surface tension of the treatment solution as shown in Figure 2, and produces a uniform coating of the fiber surface with polymer molecules to which some lauryl sulfate ions are undoubtedly bound [Fig. 3(b), Imm I]. Desorption of the surface active complex during the wetting force measurement (first immersion) produces a hydrophobic surface [Fig. 3(b), Imm II] similar to the one shown in Figure 1(c). This suggests that the polymer–surfactant complex may have been deposited on the fiber in mul-
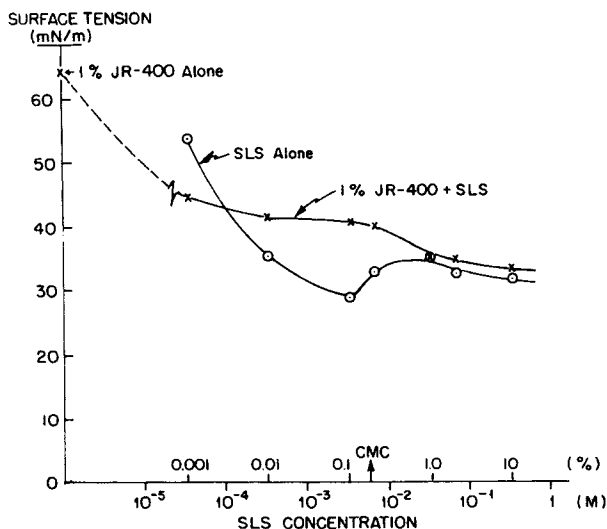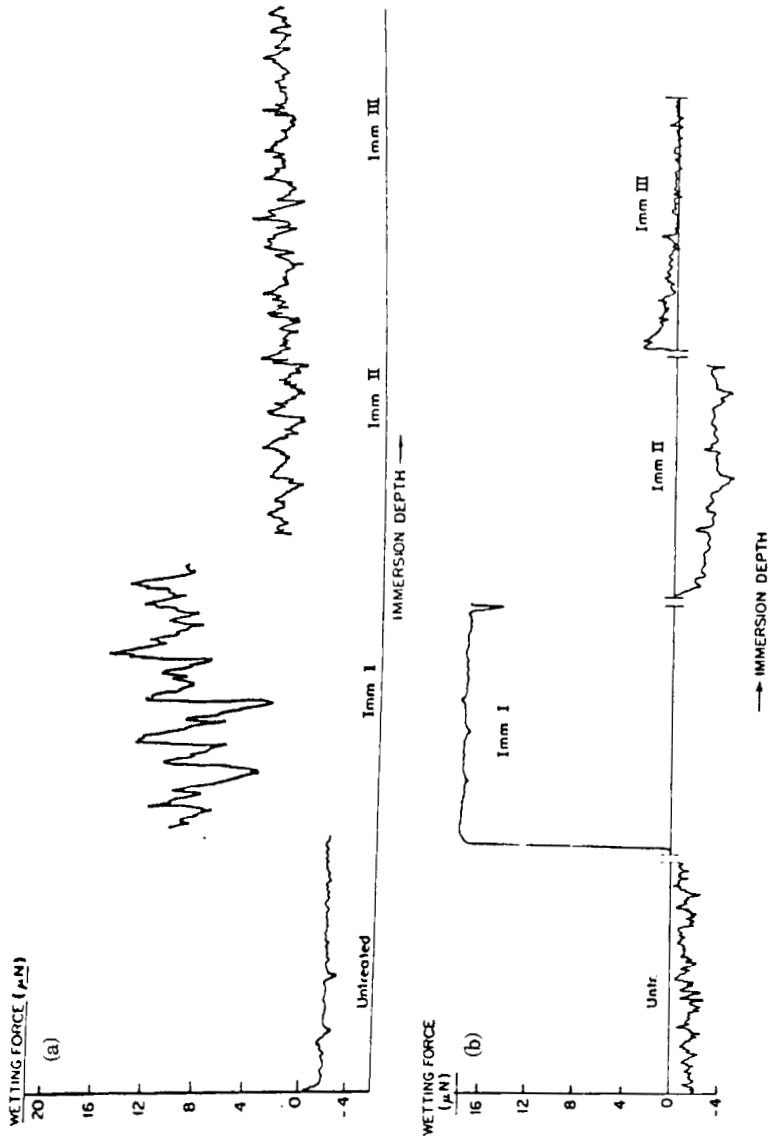

Fig. 2. Surface tension of 1% JR-400 solutions containing various concentrations of SLS.
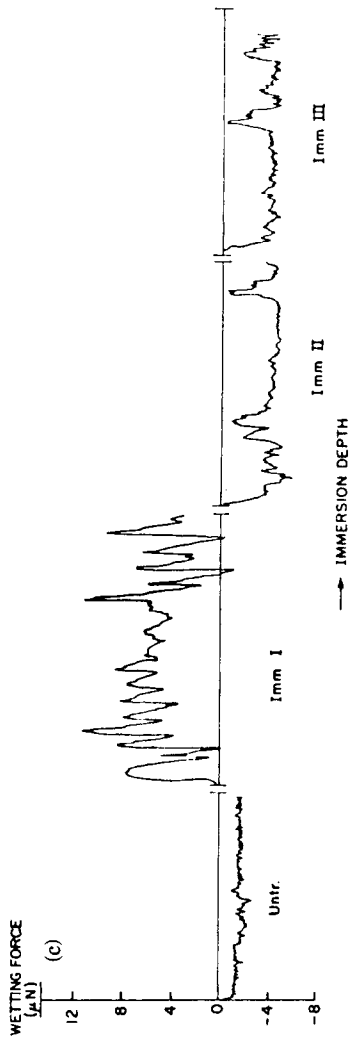
Fig. 3.   Wetting force curves for hair fibers treated with 1% JR-400 solutions containing various amounts of SLS: (a) 0% SLS; (b) 0.1% SLS; (c) 2% SLS.

timolecular layers, most of which desorb in the first immersion leaving the one closest to the solid surface.

At the higher level of SLS (2%) in the JR-400 solution, the first immersion curves show substantial variation in the wetting force [Fig. 3(c)]. This could be due to an uneven distribution of lauryl sulfate molecules with their lipid chains oriented towards the liquid. In the first immersion most of the complex seems to desorb leaving a firmly adhering layer to the surface of the fiber which turns out to be hydrophobic. This can be seen from the data for the third immersion in Table I, especially at SLS concentrations of 1% and 2%. The fibers become so hydrophobic that they cannot be immersed into the liquid easily.

Average advancing wettabilities for fibers treated with 1% JR-400 solutions containing various amounts of SLS are shown in Table I and are plotted in Figure 4 as a function of SLS concentration. High wettabilities in the first immersion indicate a continuous film of the polymer–surfactant complex, upper layers of which desorb easily. Third immersion wettabilities reflect the nature of the polymer–surfactant complex which is firmly adhering to the fiber surface. In both cases, first and third immersions, the minimum in wetting force seems to be related to the nature of binding and orientation of SLS molecules with the polymer.

Triton X-400–JR-400

As a cationic surfactant, TR-X-400 is not expected to associate with polymer JR-400. It is therefore not surprising that the surface tension of JR-400 solutions containing TR-X-400 are similar in magnitude to those of TR-X-400 solutions of the same concentrations, suggesting that the two species exist independently in solution. First immersion advancing wettabilities (Fig. 5) of fibers treated with 1% JR-400 solutions containing various concentration of TR-X-400 are essentially independent of TR-X-400 concentration. In the third immersion, however, the advancing wettabilities seem to be decreasing with increase in TR-X-400 concentration, suggesting sig-
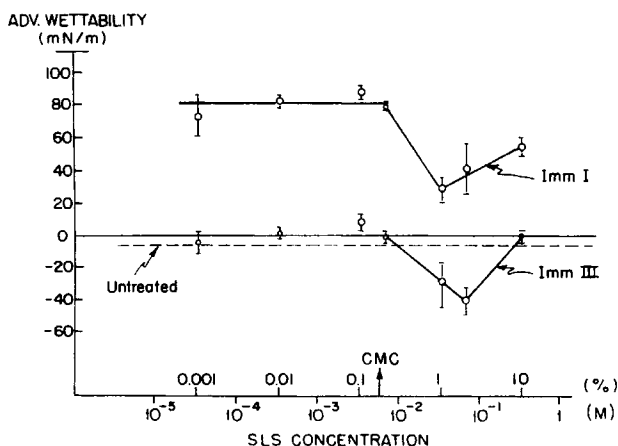

Fig. 4. Advancing wettability of hair fibers treated with 1% JR-400 solutions containing various concentrations of SLS.
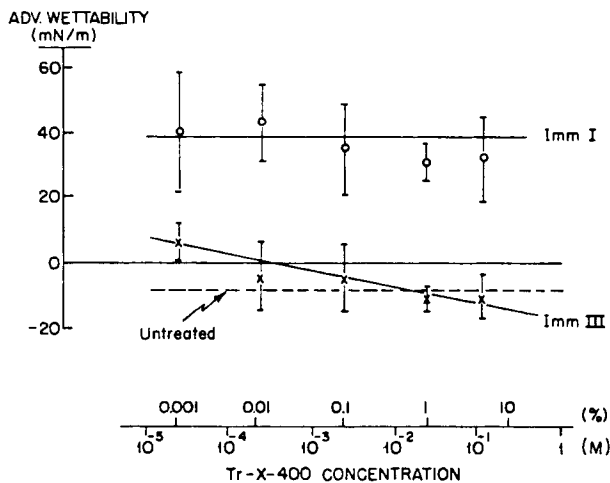
Fig. 5. Advancing wettability of hair fibers treated with 1% JR-400 solutions containing various concentrations of TR-X-400.

nificant levels of adsorption with the lipid chain oriented towards the liquid. The wetting force curves in Figure 6 show that at low concentration of TR-X-400 the polymer competes for sites on the surface, whereas at high concentration [Fig. 6(b)] the wetting force curves look similar to those of pure TR-X-400,[4] indicating that TR-X-400 competes with the polymer for surface sites almost to the point of exclusion of the polymer from the surface. Because of its smaller molecular size, TR-X-400 can adsorb much faster, thus preventing chemisorption of the polymer. This is in agreement with the observations of Faucher and Goddard,[5] who found that myristyldimethylbenzylammonium chloride drastically reduces the amount of sorbed JR-125, a polymer similar to JR-400 having a lower molecular weight.

Miranol–JR-400

Miranol C2MSF is an amphoteric surfactant with the structure
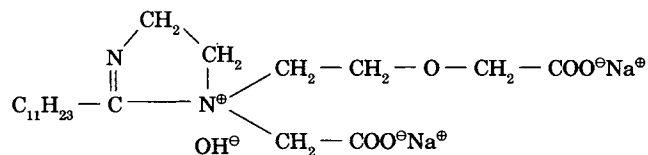
Advancing wettabilities of treated fibers in the first and third immersions are shown in Table II and Figure 7. The surface tension data seem to indicate little interaction between the surfactant and JR-400. Unlike other systems, precipitation occurs only above 10% Miranol. First immersion wettabilities are essentially independent of concentration throughout the range studied. Third immersion wettabilities in general are significantly higher than those of untreated fibers, suggesting some degree of substantivity to the surface.
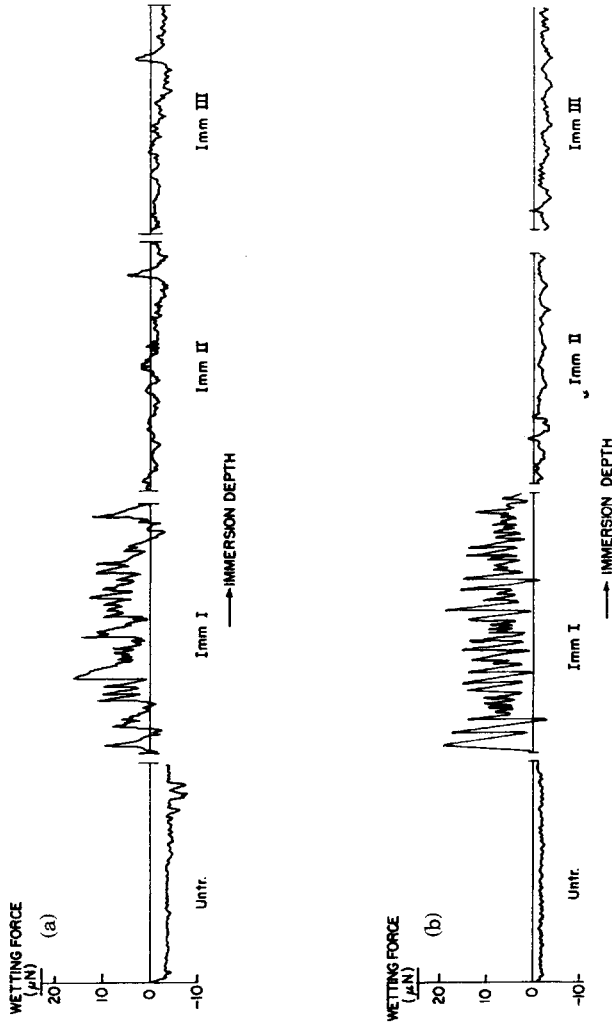
Fig. 6. Wetting forces curves for hair fibers treated with 1% JR-400 solution containing (a) 0.01% TR-X-400 and (b) 0.1% TR-X-400.

TABLE II

Advancing Wettabilities of Hair Fibers Treated with 1% JR-400 Solution Containing Various Amounts of Miranol C2MSF (Multiple Immersions in Water)

Surf. concn (%)	γ (mN/m)		Nature of solution	Advancing wettability (mN/m)[a]		
	Surf.	Polymer + surf.		Untr.	Imm I	Imm III
0		64.2	Clear, viscous	-8.4 ± 3.6	57.7 ± 14.9	13.1 ± 4.8
0.001	37.2	41.7	Clear, viscous	-5.6 ± 4.5	68.5 ± 5.0	12.7 ± 5.1
0.01	29.0	33.7	Clear, viscous	-10.9 ± 6.1	77.0 ± 4.1	11.9 ± 1.5
0.1	30.9	35.3	Clear, viscous	-10.7 ± 8.0	73.1 ± 6.7	16.0 ± 5.3
0.5	33.3	37.0	Opalescent, viscous	-10.6 ± 4.7	77.9 ± 2.3	25.9 ± 10.2
1.0	36.8	34.4	Opalescent, viscous	-1.38 ± 4.1	79.8 ± 2.9	22.9 ± 6.0
10.0	35.3	39.0	Precipitate	-4.1 ± 8.8	66.6 ± 3.1	46.9 ± 10.7

[a] Each entry is an average of six measurements at 95% confidence level.
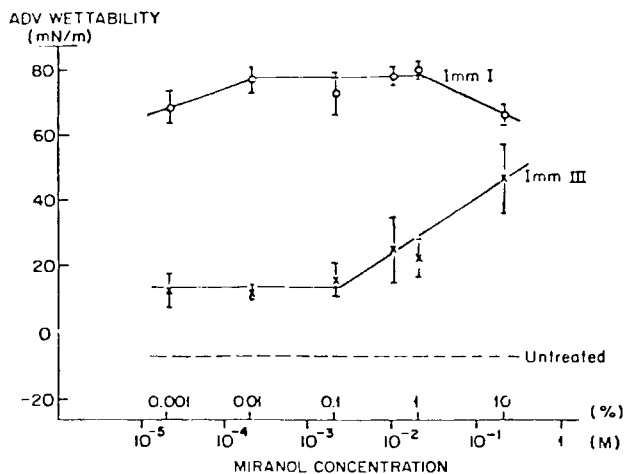
Fig. 7. Advancing wettability of hair fibers treated with 1% JR-400 solutions containing various concentrations of Miranol C2MSF.
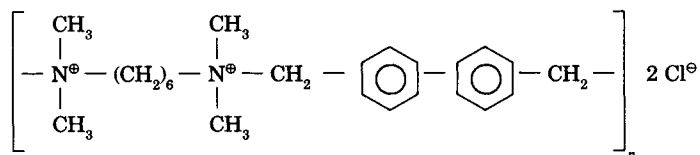
Since Miranol is an amphoteric surfactant, the interactions would be expected to depend on the pH of the polymer–surfactant solution, given in Table III. At low pH the carboxyl groups are protonated and hence are not available to complex with the polymer. At higher pH values these groups ionize and can bind with the polymer, leaving the quaternary group intact and able to bind to anionic sites on the hair surface. A trend towards increased substantivity as reflected by increases in third immersion wettability at concentrations greater than 0.1% may be associated with the increasing pH of the solution. The polymer–surfactant complex formed under these conditions, especially at high Miranol concentrations, seems to be substantive to the negatively charged surface of hair. However, the possibility of Miranol itself binding to the surface of hair at high pH cannot be ignored. This would also give rise to increased wettability in the third immersion. It should be pointed out that the wettability method in this instance cannot distinguish between the low molecular weight surfactant and the cationic polymer.

TABLE III
pH of JR-400 Solutions Containing Various Amounts of Miranol C2MSF

Miranol concn (%)	pH	
	Polymer + Miranol	Miranol
0.001	4.6	5.9
0.01	6.4	6.2
0.1	7.0	8.0
0.5	7.6	9.0
1.0	8.1	9.4
10.0	9.7	10.1

Shampoo Studies

Experimental shampoos were selected for these studies on the basis of considerable differences in their performance and substantivity as observed in beauty salon tests. It was of interest to establish whether wettability measurements in multiple immersions would substantiate these observations. Shampoos II and IV contained a cationic polymer BINA4173 with the general structure

$$\left[-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}} - (CH_2)_6 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}} - CH_2 - \hexagon - \hexagon - CH_2 - \right]_n \quad 2\ Cl^{\ominus}$$

Shampoos I and III contained no polymer but otherwise had the same composition as shampoos II and IV, respectively.

Wetting force curves in multiple immersions for hair fibers treated with these shampoos are shown in Figures 8 and 9. It was known from beauty salon tests that shampoo II containing BINA and the amphoteric surfactant Miranol C2MSF was much more substantive to hair than shampoo IV containing the same polymer but with the anionic surfactant Texapon TH. This is clearly reflected in the wetting force curves. Shampoos I and III with no polymer have only slightly higher wetting forces in the first immersion than the untreated fibers and show no substantivity to the fiber surface as shown by the second and third immersion curves. The wetting force curves for fibers treated with shampoos II and IV containing the cationic polymer show a very distinct stick–slip pattern in the first immersion, suggesting the release of surface active compounds during immersion.[4] In the case of fibers treated with shampoo II, the wetting force curves in the second and third immersions clearly show the retention of hydrophilic material on the fiber surface, most likely the polymer BINA. The increased wettability could not be attributed to the retention of the surfactant, since the wetting force curves after treatment with shampoo I show a return to the wetting behavior of the untreated fiber in the second and third immersions. Wetting force curves for fibers treated with shampoo IV show very little retention of BINA, suggesting very specific interactions between Miranol and BINA that result in greater stability of their adduct. It is interesting to note that after the shampoo IV treatment, virtually all BINA appears to be desorbed during the first immersion rather than gradually in successive immersions.

The stick–slip patterns observed for the two BINA-containing shampoos (II and IV) during the first immersion differ somewhat. For shampoo II the stick–slip phenomenon is very regular and the period (time elapsed between two consecutive maxima) is longer; for shampoo IV the fibers show a more irregular behavior with a smaller periodicity. The stick–slip behavior is a result of changes in the surface tension of the liquid at the three-phase boundary brought about by the desorption of surface active species during
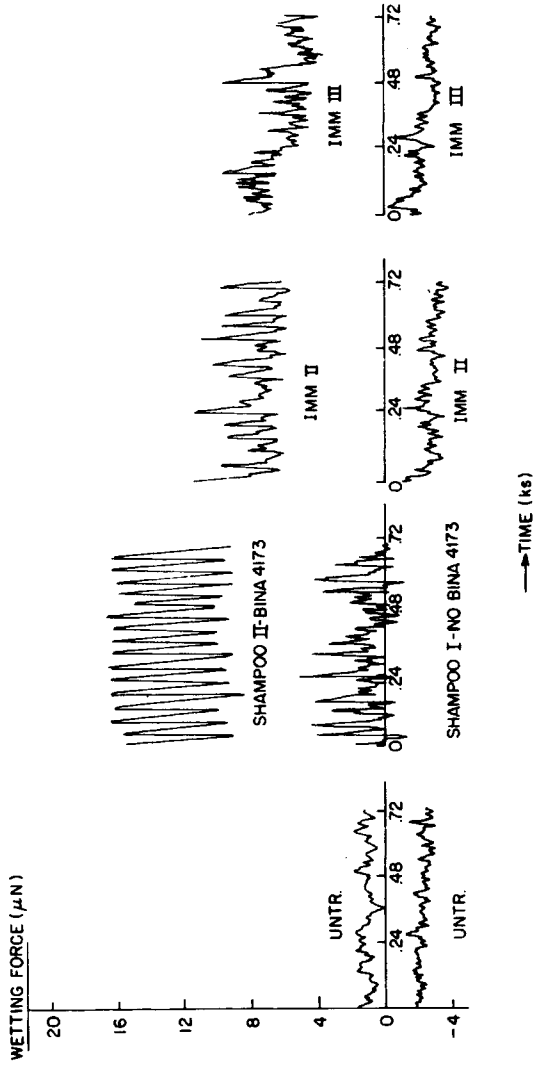
Fig. 8. Wetting force curves for hair fibers treated with shampoos I and II containing Miranol C2MSF (amphoteric).
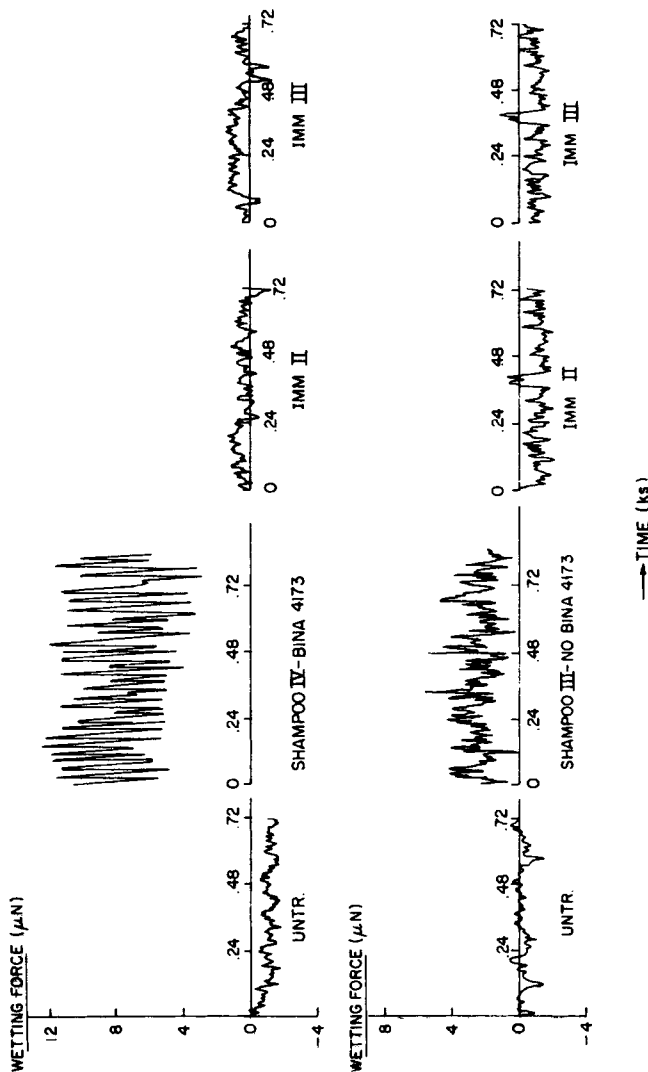
Fig. 9.   Wetting force curves for hair fibers treated with shampoos III and IV containing Texapon TH (anionic).

the measurement.[4] Therefore, the differences in the stick–slip behavior exhibited by the two shampoos probably reflect differences in the rates of desorption of surface active species from the films of the two shampoos. Desorption from shampoo II deposits appears to be significantly slower than from shampoo IV.

The differences in the behavior of formulations II and IV must be attributed to the differences in the nature of the two low molecular weight surfactants. Miranol C2MSF, used in shampoos I and II, is amphoteric, while Texapon TH, the surfactant used in shampoo formulations III and IV, is a trialkanolamine lauryl sulfate, i.e, an anionic surfactant. Interactions between surfactant and polymer probably occur between the cationic sites on the polymer and the surfactant anion. To what extent complexes are formed between surfactant and polymer and to what extent the properties of such complexes affect their deposition on the fiber surface is difficult to ascertain without a considerably more detailed investigation. It appears, however, that the association formed between Miranol C2MSF and the polymer is significantly more stable and has considerably higher substantivity to the keratin fiber surface.

Only shampoo II, i.e., the formulation containing Miranol C2MSF and the polymer, becomes opalescent upon dilution, which seems to indicate the precipitation of the polymer–surfactant complex possibly connected with decreased surfactant concentration. Indeed, one aspect of treating hair fibers with shampoos containing conditioning polymers is the extent of dilution during treatment. The adsorption of these polymeric substances is guided by polymer–solvent interactions, which are controlled by the dilution of the solution. In practical situations the shampoo is diluted *in situ* by the capillary water held between wet hair fibers. To understand the effect of dilution of the shampoo on substantivity, hair fibers were treated with shampoo II diluted to various degrees with distilled water. The average advancing wettabilities of these fibers in the first and third immersions are shown in Figure 10 as a function of the dilution ratio. It can be seen that
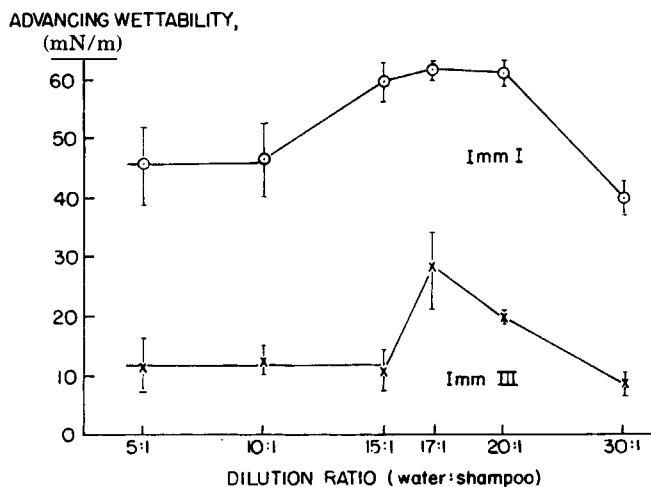

Fig. 10. Advancing wettability of water on hair fibers treated with shampoo II diluted to various extents. (Error bars show 95% confidence level.)

substantivity goes through a maximum at a dilution ratio of about 17:1. This is also the dilution ratio at which opalescence begins to appear in shampoo II solutions, the opalescence increasing as the solution is diluted further, which must be due to a phase change occurring in the solution as a result of decreasing polymer–solvent interaction. If such a phase change occurs in the vicinity of a solid surface, it would be expected that the polymer molecules would adsorb on the surface. At even higher dilution ratios, predominant polymer–polymer interactions lead to collapsing of the random coil structure and precipitation of the polymer, which can no longer adsorb on the surface of the solid with multiple points of attachment.

CONCLUSIONS

The work described in this study shows that anionic low molecular weight surfactants interact with cationic polymers to alter their adsorption characteristics on the surface of hair. At concentrations high enough to form a 1:1 complex with the cationic sites of the polymer, the surface deposited material is hydrophobic, suggesting that the lipid chains are oriented toward the liquid surface. At higher concentrations of anionic surfactant, the 1:1 complex formed initially is converted into a negatively charged polyelectrolyte by an additional hydrophobically bonded layer of surfactant molecules and hence has no affinity for the negatively charged surface of hair.

Cationic low molecular weight surfactants compete with the cationic polymer for adsorption sites, leading to a drastic reduction in the amount of adsorbed polymer. The effect of amphoteric surfactants on the substantivity of the cationic polymer seems to depend on the pH of the solution: the higher the pH, the greater the substantivity.

In addition to the nature and proportion of surfactant, the extent of dilution of conditioning shampoos containing polymeric substances during application is also found to be critical for maximum substantivity.

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