Surface Interaction of Quaternary Amines with Hair

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ABSTRACT: Surface analysis by X-ray photoelectron spectroscopy (XPS) has shown specific 1:1 (ionic) interaction between cationic alkyl quaternary surfactant molecules and the anionic sulfonate groups present on the hair surface. The primary driving force for the adsorption of alkyl quaternary amine molecules to the surface of the hair from aqueous solution is the ionic interaction between quaternary groups and the surface SO_3^- on the hair. Cationic quaternary molecules incorporating ester and alcohol functionalities (ester quats) demonstrate a lower number of surface quaternary nitrogens per sulfonate group, indicating an altered surface interaction mechanism. For the ester quats, a combination of electrostatic interaction modes exists in addition to the ionic N^+/SO_3^- interaction, specifically, H-bonding interactions of the –C–O, –C–OH, and –C(O)O– polar groups with SO_3^- and other polar groups on the hair. Surface coverage of the ester quat is not reduced despite the decrease in ionic interaction at the surface. Both types of molecules orient their alkyl tails toward the surface. Molecular dynamics modeling of the surfactant/hair surface interaction indicates higher adsorption energies due to increased dipolar interactions for ester quat molecules.

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Human hair is a complex and variable material, composed of an inner spindle overlaid with 5–10 layers of cuticle arranged like roofing shingles. Comprised of proteins, hair contains C, O, N, and S in proportion to the amino acids present. The hair surface therefore is a mix of all the possible organic functionalities present in the amino acids, (carboxylate, sulfonate, hydroxyl, amine, disulfide, thio ether, aromatic, alkyl, etc.). Crosslinks at the exterior, cuticle portion of the hair fiber are much more numerous than in the whole hair owing to the concentration of the sulfur-containing amino acid cystine. Upon aging of the hair, some of the disulfide crosslinks of cystine are oxidized, resulting in the formation of sulfonate groups at the surface (1). The carboxylate and sulfonate groups play a primary role in interactions during aqueous surface treatment owing to their charge at near-neutral pH. The isoelectric point for hair is around 3.7 (2).

Surface analysis of mammal fibers by electron spectroscopy dates back to at least 1972, when Millard studied oxidative surface treatments of wool (3). In this early application of X-ray photoelectron spectroscopy (XPS), Millard demonstrated the ability to resolve multiple chemical states of sulfur on the surface of the hair fiber. In this technique, electrons ejected by X-ray photon excitation are collected and energy-analyzed to provide quantitative elemental and chemical state data. The kinetic energy of the detected photoelectrons reflects the core-electron binding energy (binding energy = X-ray energy − measured electron kinetic energy), which is specific for the emitting element and its chemical state. Since the kinetic energy of photoelectrons is limited to the X-ray energy (typically either a characteristic Mg Kα = 1254.6 eV or Al Kα = 1486.7 eV), the transport length through the sample prior to experiencing an inelastic collision (inelastic mean free path) is short, 1–3 nm. As a consequence, the electrons finding their way out of the sample and to the detector with energies characteristic of the emitting atom emerge from no greater than ~10 nm into the sample. Overlayers on a sample surface therefore readily attenuate the substrate signal.

In this paper we discuss the mechanism of interaction of long-chain cationic surfactants with hair fiber surfaces. Specifically, we consider long-chain quaternary amine molecules based on either straight-chain saturated alkyl tails or long-chain saturated esters of triethanolamine. The goal of this work is to examine and understand the adsorption behavior of these two classes of cationic surfactants onto the surface of human hair.

EXPERIMENTAL PROCEDURES

Treatment procedure. Hair samples for this investigation were obtained from International Hair Importers & Products, Inc. (Valhalla, NY). The hair was dipped into a 1 wt% sodium lauryl sulfate soap solution and washed by rubbing between the fingers for 1 min. After being washed, the hair was thoroughly rinsed with distilled water. The washed hair tress sample was then divided into two samples, one was set aside to dry for the blank, the other for the treatment.

The washed hair was dipped into a 1 wt% solution of the quaternary surfactant, then rubbed between the fingers for 1 min. Hair was thoroughly rinsed with distilled water and allowed to air dry.

Treatment chemicals and sources. The alkyl quats employed in this study were obtained from Akzo Nobel Surfactants America (Dobbs Ferry, NY). The alkyl chain length for all materials was nominally C_{16}, $[(H_3C)_{4-x}N^+–(C_{16}H_{33})_x]Cl$ (x = 1–3). The ester quat composition was 25% mono, 65% di, and 10% triester based on NMR analysis, $[H_3CN^+ –(C_2H_5–OH)_{3-x}–(C_2H_5–OC(O)C_{15}H_{31})_x]Cl^-$ (x = 1–3).

XPS. XPS spectra were collected at room temperature with a Physical Electronics (Eden Prairie, MN) 5600ci electron spectrometer. Excitation of the sample was accom-

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plished with a monochromatic Al Kα X-ray source (hν =1486.7 eV, 300 W) producing an approximately 7 × 3 mm illuminated area on the sample. Photoelectrons from a 0.8 × 0.8 mm area were energy-analyzed with a 279 mm mean diameter hemispherical electron energy analyzer. The angle above the surface plane to the electron collection lens axis was 45°. Surface charge neutralization was performed with an electron flood gun source, nominally operated at 20 ma emission and 0.5 V acceleration potential. Exact flood gun conditions were optimized for each sample to obtain minimal peak width with the hydrocarbon C(1s) binding energy around 284.4–284.0 eV.

Low-resolution survey scan and high-resolution chemical state spectra were collected in fixed analyzer transmission mode at pass energies of 187.85 and 23.50 eV, respectively. Spectrometer resolution, measured as full width at half maximum of the 3d5/2 photo electron peak from Ag foil were 2.4 (187.85 eV pass energy) and 0.8 eV (23.5 eV pass energy).

Binding energy scale calibration was performed as described in the E-42 ASTM-902 document (4). The procedure employs the peak separation of the Cu(2p3/2) and Cu (3p3/2) photoelectron peaks to establish scale linearity. The Cu photopeaks and the Cu (KLL) Auger peak positions are then used to calibrate the absolute energy scale. Binding energy assignments for the charge-compensated (-shifted) sample spectra were based on an assignment of the hydrocarbon ($–CH_2–$) C(1s) component in the high-resolution C(1s) spectrum to 284.8 eV.

Samples for every analysis were taken from as near the midpoint along the length of the hair tress as could be reproducibly achieved. Hair fibers were mounted between two three-hole sample cover masks (Physical Electronics part # 612448), which held the fibers co-planar and parallel. Double-sided tape was placed on either side of the holes on the lower mask, and the fibers (~20), cut to about 2 in. (~5 cm) in length were placed and pressed onto the tape across the hole. The second mask was placed above the first, and screws were run through both masks into the recessed sample mount (Physical Electronics part 606142) securing the fibers in place. The sample mount was placed within the spectrometer so that the hair fibers were oriented parallel to the source-analyzer plane.

Instrument control, data collection, and data analysis were all performed with Physical Electronics PC-ACCESS software running on a Pentium PC. Quantitation calculations were based on measured peak areas and empirical instrumental sensitivity factors within the above-mentioned software. Curve-fitting analysis employed a linear background and a mixed Gaussian–Lorentzian peakshape.

The XPS technique is capable of observing every element except H and He. In the Results and Discussion sections of this paper molecular formula will be expressed in terms of C, O, N, and S. Compositions will be expressed on a 100% basis considering only C, O, N, and S.

Molecular dynamics. Comparative molecular absorption energies of monoalkyl quat and diester quat surfactants were generated by the following method. A model of the cuticle surface was generated by building fifteen 20-mer polypeptide chains. The sequence of the chains was randomly chosen within the constraint of the cuticle residue content reported in Reference 1 (p. 14). The peptide backbone torsion angles were then adjusted to that for a beta pleated sheet. The chains were docked side-by-side, and the resulting structure was energetically minimized by Cerius2 software (Molecular Simulations Inc., Princeton, NJ) to maximize interchain hydrogen bonding in the beta sheet. The target surfactant molecule was then docked 10 Å above the center of the peptide sheet with its alkyl chain(s) normal to the sheet. The interaction energy was maximized by Cerius2's method of quenched molecular dynamics. For each initial position, 25 cycles of 2.5 nanoseconds of molecular dynamics–energy minimization was performed with the peptide sheet position held fixed. Positions and energies of the surfactant molecule–peptide sheet pair were automatically saved for each cycle. The target molecule was positioned at four additional sites over the sheet and the quenched dynamics simulation performed. These positions were then repeated on the reverse side of the sheet, yielding a total of 10 different local environments. The resulting data were analyzed to determine the maximal interaction energy of each local environment with the contribution of the van der Waals, electrostatic, and hydrogen-bonding energies separately tabulated.

RESULTS

Blank hair. The average composition and SD of the blank hair surface from 10 separate samples was found to be 73.5 ± 2.2 atom% C, 17.2 ± 1.2 atom% O, 7.3 ± 1.2 atom% N, and 2.0 ± 0.2 atom% S. A representative survey scan is shown in Figure 1. Note that in Figure 1, the 2s (~230 eV) and 2p (~185 eV) photoelectron transitions from S are present. Each of these S photoelectron transitions comprises two resolved peaks owing to the disulfide (–S–S–) links of the cystine amino acid and sulfonate ($–SO_3^-$) ion (Fig. 2). The formation of sulfonate groups is restricted to the outermost surface, where atmospheric oxygen and UV illumination interact with the hair fiber (1,4). The observed nitrogen is present in a single chemical state (399.8 eV), owing to the amide (peptide) links between amino acids. Calcium and silicon were observed as naturally occurring constituents of the hair, and were present in low levels (<1.0 atom%), consistent with previous work (5).

The uncertainties in the average blank hair surface composition noted above are an indication of the variability of the hair fiber surface from one sample tress to the next. Each analysis is only representative for the specific area of analysis, for the surface composition (chemistry) changes with position along the fiber length (5,6). Most notable of the observed changes is the increase in the amount of sulfonate present relative to disulfide from root to tip (5). For this reason a blank from the same hair tress was run along with each treated sample. The sampling position along the length of the hair fiber taken for the treated sample and blank was kept as consistent as possible.

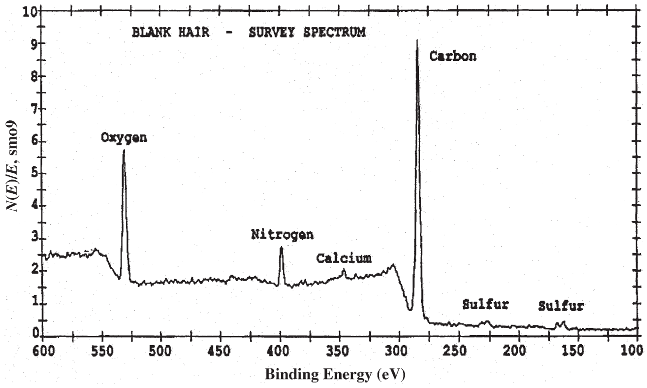

FIG. 1. Survey scan of untreated hair fibers. *N*(*E*)/*E* refers to the number of electrons as a function of energy over kinetic energy of the electrons; smo9 indicates that data were smoothed using a nine-point smoothing function.

Alkyl quaternary amine-treated hair. Treatment of the hair fibers with 1% aqueous solutions of alkyl quats $[(H_3C)_{4-x}N^+\text{–}(C_{16}H_{33})_x]Cl^-$ (x = 1–3) resulted in the formation of an adsorbed surface layer readily observed by the XPS analysis. The appearance of a N(1s) peak at 402.1 eV, characteristic of N^+ quaternary nitrogen (Fig. 3), indicated the presence of the surfactant on the hair. Adsorption of the alkyl quats onto the hair changes the net composition observed by the surface-specific XPS analysis (Table 1).

In no case was there evidence for retained chloride (Cl^-) from the original chloride salt of the quaternary compounds. The absence of the anionic chloride at the surface indicates the solvated chloride did not interact with the hair surface (hair surface possesses a net negative charge at neutral pH, isoelectric point = 3.7) and was washed away with the water rinses. In addition, the absence of negatively charged counter-ion indicates that multilayer formation through alkyl tail association did not occur.

To more clearly illustrate the changes that occurred with the differing alkyl quat treatments, Table 2 lists changes in surface composition relative to the specific blank from each sample preparation. The values were determined by taking the difference between the surface composition results and the corresponding blank fiber for each analysis of each treatment. The elemental composition changes from each blank/treated sample pair (for a specific treatment) were averaged to obtain the values in Table 2.

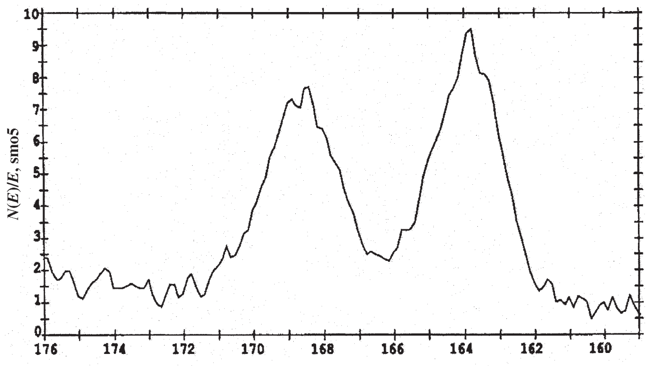

FIG. 2. High-resolution spectrum of the S(2p), illustrating the presence of the sulfonate and disulfide chemical states. Sulfonate peak 168.6 eV, disulfide peak 163.8 eV. For abbreviations see Figure 1.

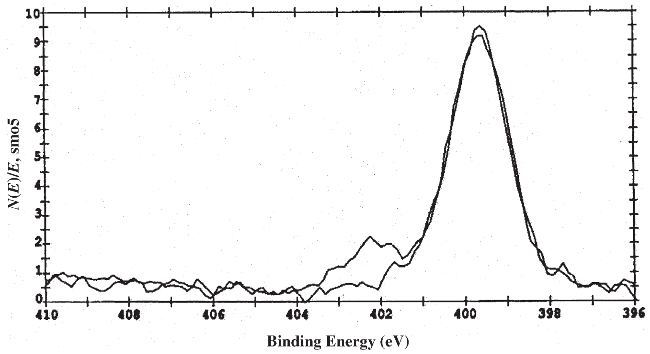

FIG. 3. High-resolution N(1s) spectrum of monoalkyl treated hair. Quaternary nitrogen peak = 402.1 eV, amide nitrogen peak = 399.3 eV. For abbreviations see Figure 1.

Another illustration of the change in the surface composition is found in the abundance of the various chemical states of carbon. Curve fitting of the high-resolution C(1s) data was performed for each of the alkyl quat-treated hair samples and corresponding blank. The C(1s) spectrum was fitted with three components assigned to carboxyl, C–O, or C–N bonding, and alkyl C–H bonding. As in Table 2, the differences between the treated sample and the blank were determined and averaged over each of the treated sample/blank pairs for a specific treatment (Table 3).

Coverage and layer thickness of the monoalkyl treatment were examined by calculating theoretical XPS compositional results in comparison to the experimental data. Known composition of the hair (blank sample results) and the monoalkyl quaternary amine were used in the classic substrate–overlayer approach (7) to predict surface composition based on presumed surface structures. The possible range of layer thickness for a C_{16} alkyl chain was assumed to be 2.2 nm (~0.14 nm/CH_2) (8) when fully extended normal to the surface or 0.15 nm when lying completely flat on the surface. Electron inelastic mean free paths from Tanuma *et al.* (9) were employed in these calculations.

The results of the structure modeling calculations (Table 4) suggest two potential surface coverage structures representative of limiting cases. The first limiting case is a partial coverage of the surface with a full-height alkyl chain normal to the surface plane. The second limiting case consists of a full layer with a thickness greater than that expected if the layer were completely flat on the surface. Note that these two suggested solutions for the structure represent the

TABLE 1
Elemental Composition of Treated Hair Fiber Surfaces

Element	Blank[a]	Monoalkyl quat[b]	Dialkyl quat[b]	Trialkyl quat[b]
C	73.5 ± 2.2	77.9 ± 0.3	76.4 ± 2.0	79.7 ± 0.2
O	17.2 ± 1.2	13.3 ± 0.4	13.5 ± 0.8	12.5 ± 0.8
N	7.3 ± 1.2	6.7 ± 0.3	8.0 ± 0.8	6.2 ± 0.4
S	2.0 ± 0.2	2.1 ± 0.2	1.9 ± 0.4	1.6 ± 0.3

[a] Mean of 10 analyses and SD from several differing hair tresses. Uncertainty of these data reflects the natural variation in the hair surface.
[b] Mean of three analyses and SD.

TABLE 2
Average[a] Elemental Composition Change of the Treated Samples Relative to the Corresponding Blank

Element	Monoalkyl quat	Dialkyl quat	Trialkyl quat
C	+3.4	+5.6	+8.3
O	–3.8	–4.6	–0.5
N	+0.2	–0.3	–2.6
S	+0.3	–0.4	–0.6

[a] Three values averaged for the mono- and trialkyl quats, two values averaged for the dialkyl quat.

boundary conditions of a multitude of intermediate solutions that fall between the limiting cases. The important criterion to impose on any of these potential solutions is that of physical rationality and consistency with other data.

Curve fits of the N(1s) and S(2p) spectra permit the extension of Table 1 to include values for specific nitrogen and sulfur chemistries present on the surface. Of particular interest is the relation between the N^+ of the quaternary amine and the hair $–SO_3^-$ surface group. Table 5 lists the curve fitting results in terms of surface atom% for these specific functional groups.

The data in Table 5 strongly suggest that the quaternary nitrogen adsorbs preferentially and proportionally to the negatively charged surface sulfonate groups. Sulfonate concentrations from blanks are included to demonstrate the consistency of results of samples from a single hair tress. The similarity of the sulfonate data for both the treated and untreated (blank) samples indicates that the treatment process does not alter the hair and that the chosen analysis areas for the treated and blank portions of the tress are of consistent surface chemistry.

Ester quaternary amine-treated hair. In addition to a quaternary nitrogen, ester quats $[H_3CN(^+)C_2H_5O–(C(O)C_{15}H_{31})_x(H)_{3-x}]Cl^-$ ($x = 1–3$) have oxygen-containing functionalities that contribute to the O(1s) and C(1s) spectra. In comparison to the mono alkyl quat, the ester quat-treated hair shows increased intensity in the 286–289 eV portion of the C(1s) spectrum, corresponding to the ester quat C–O and COO structures (Fig. 4).

In Table 6 are listed the surface compositional changes of the ester quat-treated hair samples in comparison to the blanks. The alterations in the surface composition are very modest, and Table 6 alone does not clearly indicate the presence of a surface layer. The absence of a dramatic change in the surface composition with ester quat adsorption is due to the similar compositions of the ester quat and the hair fiber. The composition of the ester quat can be expressed as $C_{0.86}O_{0.114}N_{0.023}$, whereas that of the blanks collected in conjunction with the ester quat samples had an average composition of $C_{0.734}O_{0.172}N_{0.072}S_{0.022}$. The compositions of the alkyl quats were quite different from the hair in general, with no O and the molecular formula of $C_{0.95}N_{0.05}$. As a result, a surface layer of the alkyl quats had a much greater effect on the overall measured composition. Since the changes in surface composition with ester quat adsorption were so small, the results of model surface composition calculations were inconclusive with regard to layer thickness and coverage.

TABLE 3
Average Change in Carbon Chemical State Between the Treated Sample and Corresponding Blank

Chemical state	Monoalkyl quat	Dialkyl quat	Trialkyl quat
Carboxyl, (COO)	–0.8	–2.5	–2.5
C–O/C–N	+4.5	+1.7	+0.6
Alkyl, $–CH_2–/–CH_3$	–0.2	+6.4	+10.3

TABLE 4
Predicted XPS Surface Composition[a] Assuming a Monoalkyl $C_{16}H_{33}N^+(CH_3)_3$ Overlayer of Differing Surface Thickness and Coverage

Coverage	Thickness (nm)	Carbon	Oxygen	Nitrogen	Sulfur
Measured		**77.9 ± 0.3**	**13.3 ± 0.4**	**6.7 ± 0.3**	**2.1 ± 0.2**
0	Blank	74.4	17.2	6.5	2.0
0.1	2.2	75.7	16.1	6.4	1.8
0.2	2.2	76.9	15.0	6.3	1.7
0.3	**2.2**	**78.2**	**13.9**	**6.3**	**1.6**
0.5	2.2	80.7	11.8	6.1	1.4
0.8	2.2	84.5	8.5	5.8	1.1
1	2.2	87.1	6.4	5.7	0.9
1	1.905	86.0	7.3	5.7	1.0
0.5	1.905	80.2	12.2	6.1	1.5
0.3	1.905	77.8	14.2	6.3	1.7
0.2	1.905	76.7	15.2	6.3	1.8
1	1.556	84.5	8.5	5.8	1.1
1	1.1	82.2	10.5	6.0	1.3
0.5	1.1	78.3	13.8	6.3	1.6
1	0.45	78.0	14.0	6.3	1.7
1	0.15	75.7	16.0	6.4	1.9
0.8	0.15	75.4	16.3	6.4	1.9
0.5	0.15	75.0	16.6	6.5	1.9
0.2	0.15	74.7	16.9	6.5	1.9
0.1	0.15	74.5	17.0	6.5	1.9

[a] Tilting of the alkyl tail would result in cases of intermediate layer thickness; 1.905 nm would result from a 30° tilt from normal, 1.556 nm from a 45° tilt, 1.1 nm from a 60° tilt, and 0.45 nm from a 78° tilt. XPS, X-ray photoelectron spectroscopy. Boldface values indicate parameter combinations that closely approximate measured values.

Examination of the C(1s) high-resolution data, provided the following data regarding the average change in carbon chemical state between the ester quat-treated samples and corresponding blank: carboxyl, COO, +1.6 atom%; C–O/C–N, +7.4 atom%; alkyl, $–CH_2–/–CH_3$, –8.7 atom%. Together with the illustrations of Figure 4, these data more clearly indicate the existence of a significant surface layer of the ester quat.

The ester quat N^+ nitrogen to SO_3^- ratio was found to be 0.6, which is significantly lower than that observed for the alkyl quat treatments where the ratio was essentially 1. The change in the N^+/SO_3^- ratio indicates that in the case of the

TABLE 5
Curve Fitting Results[a] of N(1s) and S(2p) XPS Spectra (atom% of surface composition)

	Monoalkyl quat	Dialkyl quat	Trialkyl quat
N	1.1 ± 0.1	0.8 ± 0.2	0.7 ± 0.1
SO_3^- Treated	1.2 ± 0.1	0.8 ± 0.1	0.6 ± 0.1
SO_3^- Blank	0.9 ± 0.2	0.7 ± 0.1	0.7 ± 0.1

[a] Values are mean and SD from three separate analyses. For abbreviation see Table 4.

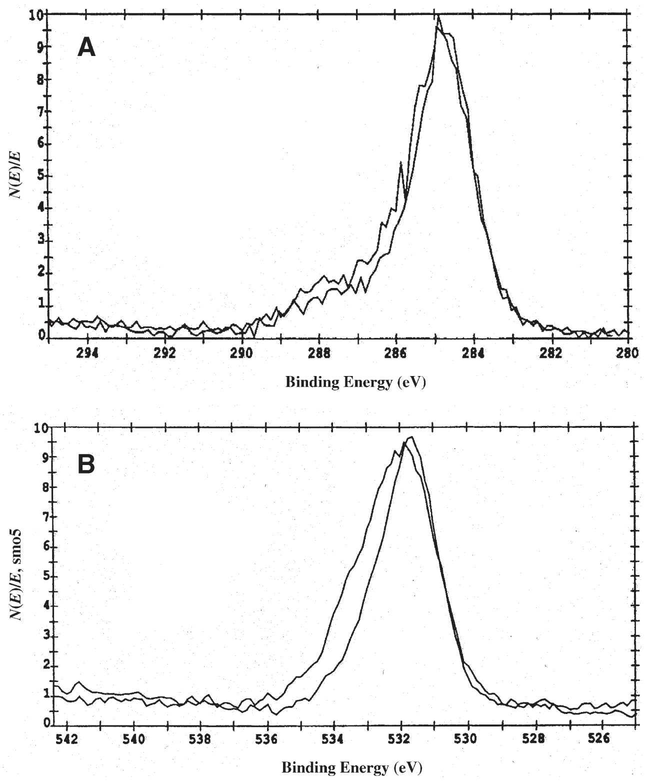

FIG. 4. (A) Carbon (1s) overlay spectrum showing enhanced intensity in the C–O (286.2 eV) and C=O (288.0 eV) region of the spectrum from the ester quat-treated hair in comparison to the alkyl quat-treated hair. Main C(1s) peak ($-CH_2-$) = 284.8 eV. (B) Oxygen (1s) spectral overlay of ester quat- and alkyl quat-treated hair. Ester quat displays a broadened peak at ~533.5 eV due to increased amount of C–O bonding. For abbreviations see Figure 1.

ester quat, site-specific ionic adsorption is not solely responsible for the observed adsorption.

Comparison of Tables 3 and data above on the average change in the carbon chemical state illustrates the difference in the nature of the adsorbing films. In Table 3 the alkyl component of the C(1s) spectrum is either constant or increasing, reflecting the predominant C–H nature of the alkyl quats. The alkyl component of the carbon chemical state (cf. material above) decreases due mainly to the large proportion of C–O and C–N bonding states in the ester quat. The ester quat also shows an increase in the carboxyl content as a result of the ester functionalities. Carboxyl content observed from the alkyl quat-treated samples (Table 3) decreases as the surfactant layer becomes more alkyl in nature.

Molecular dynamics calculation/simulation. Calculated interaction energies between a representative hair fiber surface and the quaternary surfactants are summarized in Table 7. The significant increase in calculated interaction energy for the ester quat is a result of H-bonding of the polar –C–O–, –C–OH, and >C=O structures with the hair surface. Polar group interactions contribute to the electrostatic term, which is clearly greater for the ester quat. The H-bonding term listed in Table 7 represents the additional energy found in the unique H-bonding interaction not accounted for by the electrostatic term. Again there is only a H-bonding term for the ester quat. These calculations support the hypothesis from the XPS data that additional modes of interaction are present between the ester quat and the hair.

TABLE 6
Surface Composition of Ester Quat-Treated Hair, and Composition Change in Individual Runs

Element	Mean of treated hair composition	Composition change (atom%)
C	73.7	+0.2
O	16.6	–0.5
N	7.3	+0.1
S	2.2	–0.1

TABLE 7
Calculated Interaction Energies (kcal/mol)

	Monoalkyl quat	Dialkyl quat	Ester quat
Van der Waals	–8.03	–11.2	–8.31
Electrostatic	–41.08	–44.09	–68.76
H-Bond	0.0	0.0	–1.62
Total	–49.11	–55.29	–78.69

The Van der Waals association energies calculated are all very similar, suggesting that the alkyl chains of these molecules behave similarly. The energy-minimized orientation of the alkyl tail was lying along the hair surface although not uniformly flat along the full alkyl chain length (Fig. 5). An orientation of the alkyl tail near the surface would favor the high coverage, low thickness limiting case from the XPS attenuation calculations presented above.

DISCUSSION

The forces responsible for the adsorption of the quaternary amine molecules can be represented by the terms utilized in the molecular dynamics calculations, e.g., van der Waals, electrostatic, and H-bonding (10). The electrostatic term is composed of both ionic and dipolar interactions. The ionic interaction is very dependent on the pH of the treatment solution. Carboxylic and sulfonic acid groups exist on the surface of the hair; however, the carboxylic acids are much weaker (on average, 3 pK_a units) than the sulfonic acid sites (11). Since the sulfonate (sulfonic acid, $pK_a \sim 3–5$) groups are fully ionized at the neutral pH of the treatment solutions, these sites would be expected to dominate the ionic surface interactions.

The ester quat –C–O–, –C–OH, and –C=O structures introduce dipolar interaction modes with the hair surface beyond that of the quaternary N^+. As a result, ester quat molecules are not solely dependent on the surface sulfonate concentration as a means for adsorption. The ester quats can interact at multiple sites, whereas the alkyl quats can only adsorb to the surface through the charged quaternary nitrogen with the charged surface sulfonate site. During the adsorption process the alkyl quat would need to migrate along the surface to find the charged sulfonate site. The multiple-site interaction capability of the ester quat means that more than one surface sulfonate can be charge compensated by a single ester quat molecule and not necessarily by the N^+. Negatively

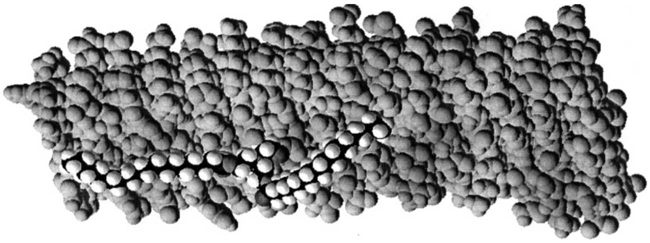

FIG. 5. Molecular dynamics simulation of ester quat adsorption onto hair surface.

charged surface sulfonate groups can interact with either the positively charged quaternary nitrogen or the proton of the nonesterified alcohol (–OH) groups. Therefore, the low N^+/SO_3^- ratio for the ester quat is a direct consequence of the multiple modes of interaction with the hair surface.

The van der Waals interactions of the alkyl tail with the hair surface can be thought of in energy minimization terms. The system energy can be minimized by removing the alkyl tail from the polar water solution onto the surface of the hair. The molecular dynamic calculations were performed in the absence of the explicit presence of water; however, hydrophobic forces would be expected to increase the stabilization on the surface. As observed in the molecular dynamics results, the energetic contribution by the van der Waals interaction is relatively equivalent for the two types of materials tested. The trialkyl quat shows the same 1:1 N^+/SO_3^- relation as the monoalkyl quat, indicating that the alkyl tails on the surface do not interfere with the ionic interaction of the alkyl quats, either energetically or sterically.

The absolute coverage of the hair surface is difficult to assess. The calculation results above yield a range of possible surface coverages and structures that approximate the observed experimental results. Additional information must be brought to bear to be more specific. One possible rationalization for coverage with a thickness greater than a single layer would be the adsorption of molecular assemblages on the surface. At a concentration of 1% the existence of micelles in the treatment solutions is ensured. However, based on the experimental data, the presence of immobilized micelles does not seem consistent with the data. The fact that the mono-, di-, and trialkyl quats all show 1:1 interaction by ionic association with the surface demonstrates that the potential associative forces of the alkyl tails is insufficient to maintain molecular assemblies. The 1:1 ionic association could only take place if the surfactant molecules could migrate freely and individually to the surface site of greatest associative strength. The absence of residual chloride also precludes the presence of multilayer adsorption. Multilayers would result in the presence of unassociated quat. Chloride would need to be present to compensate for the N^+ charge of such unbound molecules. Aggregates or micelles may indeed adsorb to the surface initially from the treatment solution, but subsequent steps would probably include cluster dissociation, molecular dispersal across the surface, and association and desorption of nonbound molecules during the rinse.

An overlayer thickness of 0.45 nm is the minimum value from the calculations at full surface coverage. One possible explanation for this result is the presence of a kinked hydrocarbon layer produced by the alkyl tail(s), making for an increased average height above the surface. The molecular dynamics results indicate that such structures are possible even in a fully energy-minimized configuration. Kinking of the alkyl chain could be a reflection of the local hydrophilic–hydrophobic nature of the hair surface. Certain amino acids have polar (hydrophilic) side chains, whereas others have nonpolar (hydrophobic) side chains. As a result there will be localized areas of the surface where the alkyl chain will find interaction favorable and others where it is nonfavorable.

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