Interactions of cationic and anionic surfactants on hair surfaces: Light-scattering and radiotracer studies

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Synopsis

Light-scattering techniques, supplemented by radiotracer studies, have been used in this work to demonstrate formation on hair surfaces of insoluble complexes between some common cationic conditioner actives and anionic lauryl and laureth sulfates. These complexes, which were found to be very dulling and resistant to cleaning by C12-based detergents, were shown to form in tress treatments and also in treatments of full heads of hair.

Alkyl ether sulfates having hydrophobic chain lengths of 6, 8, or 10 were found not to form the above types of complexes on hair and were shown to be superior for use in cleaning conditioners. In experiments with conditioner actives, contributions to buildup were found from both conditioner and detergent deposition. In the case of commercial conditioners, buildup was observed only as a result of excess detergent deposition in the presence of conditioner. In both cases, formation of insoluble complexes led to greatly reduced cleaning by lauryl or laureth sulfate-based shampoos.

INTRODUCTION

In a previous paper, Reich and Robbins (1) described the use of light-scattering techniques to follow cleaning and soiling of the hair surface.

Using the demonstrated techniques, along with dye staining methods, it was shown that complexes could form on hair between Polyquaternium-10 cations and myristate anions when these two species were deposited on the hair from different shampoos. Formation of these complexes was shown to have a negative effect since the resultant deposits were very dulling and quite resistant to removal from the fiber surface.

In work previous to the above, Robbins *et al.* (2) demonstrated the formation of a different type of complex on hair, between cationic stearalkonium chloride (SAC) or cetrimonium chloride (CTAC) particles and conventional, anionic shampoo detergents. The former two species are conditioner actives commonly found in many commercial conditioners.

Because of the nature of the techniques used in reference 2 to establish complex formation, dye staining and radiotracers, it was not possible to say much concerning the effects on hair of complex formation. In addition, although the possibility of complex

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formation was investigated for a large number of detergents, the relative efficacy of most of these detergents in cleaning conditioner soil was not established.

In this paper, it is shown that the light-scattering techniques described in reference 1 can be used to rapidly and conveniently answer the above questions concerning conditioner/detergent interactions on hair.

As in reference 1 for shampoo complexes, it is shown, using light scattering, that conditioner:detergent complexes formed on the hair are very dulling and difficult to remove with common detergents. These effects are shown to be readily measured on single fibers, on hair tresses, and even on full heads of hair.

Following this, surfactants not exhibiting formation of insoluble complexes on hair are presented, and the relative conditioner cleaning efficiencies of a large number of surfactants is determined.

The above measurements are performed with both conditioner actives and fully formulated conditioners. The results from both types of experiment are confirmed and supplemented with more detailed radiotracer experiments than were run in the previous work.

The results in this paper show that light scattering can be used to rapidly and quantitatively measure the practical effects on hair of many hair care products. As was stated previously (1), much of this type of information would be difficult or impossible to obtain using other techniques.

EXPERIMENTAL

TRESS PREPARATION

All tresses were prepared with three grams each of human hair purchased from DeMeo Brothers, New York. In order to minimize scattering from the interior of the hair, only virgin, Oriental hair was used (1).

Permed tresses were prepared by perming 60-gram bundles of hair with a standard commercial perming product. After the initial perm, the hair was washed twice with a 20% solution of SODS, a detergent consisting of 45% sodium octeth-1 sulfate and 55% sodium deceth-1 sulfate (Vista Chemical Co., Austin, TX). Following this treatment, the hair was permed and washed again, and then divided into three-gram tresses.

TRESS TREATMENTS

For all comparison series, a minimum of three tresses was prepared for each treatment. In addition, three control tresses, treated only with 20% SODS and representing "clean hair," were prepared for each series. When carrying out a comparison experiment, succeeding tresses in a series received different treatments so that any particular treatment was staggered throughout the entire series.

For stearalkonium chloride (SAC)/detergent experiments, tresses were subjected to two prewashes, followed by three treatment cycles. In commercial conditioner/detergent experiments, the number of treatments was increased to five.

Prewashes were performed by applying 5 ml of 20% SODS to a tress, rubbing by hand for one minute, and then rinsing for one minute under running tap water at a temperature of 100° F.

Treatment cycles for SAC/detergent experiments consisted of treatment with 2 ml of 1% SAC in a 30:70 ethanol/water mixture, rinsing, treatment with 0.5 ml of a 20% solution of a test detergent, and then another rinse. Each treatment solution was rubbed into the tress for one minute, while each rinse was carried out under 100° F running tap water for one minute.

Commercial conditioner/detergent experiments were run in the same fashion as above, except that treatment quantities were increased to 5 ml of conditioner and 2 ml of detergent.

HALF-HEAD TESTS

Half-head tests were carried out by parting a panelist's hair down the middle and subjecting each half to different treatments. All treatment samples in each test were rubbed into the hair for one minute, while the duration of all rinses was also one minute.

All half-head tests were begun by washing each side of the head with 5 ml of the test shampoo (detergent) to be used on that side. This was performed twice, followed by a rinse each time.

Following the above, both sides of the head were treated with either 15 g of 6% SAC in a 30:70 ethanol/water mixture or 15 g of a commercial conditioner. This treatment was followed by a water rinse, after which each side of the head was treated with 5 ml of either 20% SODS or 20% triethanolamine lauryl sulfate (TEALS) and then rinsed again. The entire conditioner/surfactant cycle was repeated three times.

For SAC experiments, 30–40 hairs were taken from each side of the head after the last shampoo and put aside for light-scattering measurements. The hair was then blow-dried, combed as straight as possible to avoid orientation artifacts, and evaluated subjectively.

All subjective evaluations were carried out in a darkened room under an overhead point source lamp (Smith-Vicker #710 lamp; Sylvania FBD, 500-watt bulb) by four to six trained evaluators. Note that, of the evaluators, only the hairdresser knew which treatment each side had received.

For commercial conditioner experiments, the procedure followed was the same as the above, except that, in most cases, sampling and subjective evaluation were carried out after both the last conditioner and the last detergent treatments.

RADIOTRACER EXPERIMENTS

$[^{14}C]$SAC, $[^{14}C]$CTAC, $[^{35}S]$ammonium lauryl sulfate (ALS), $[^{35}S]$sodium deceth-2 sulfate (SDES-2), and $[^{35}S]$sodium deceth-3 sulfate (SDES-3) were all synthesized in the radiotracer laboratories at Colgate. The precursor alcohols for the last two surfactants in the preceding list were provided by Vista Chemical Co., Austin, TX.

The above radiolabeled compounds were diluted in their non-radioactive counterparts so that the final activities were between 0.1 and 0.3 microcuries per gram of solution.

Wool swatches (7.6 × 11.4 cm wool challis, Test Fabrics, Inc., Middlesex, NJ) were prepared for radiotracer experiments by overnight immersion in a 1:1 mixture of acetone and ethanol. Following overnight drying, the cleaned swatches were cut with pinking shears into 0.14-g segments having areas of approximately 8.4 cm^2. At least five of the cut segments were prepared for each treatment under study.

In all experiments, cut swatches were wetted with tap water, excess water squeezed out, and the swatch laid on a stainless steel wire gauze placed over a beaker. Following this, either 0.3 or 0.15 ml of a test material was applied to the swatch as evenly as possible. The wool was then rubbed for one minute between two lengths of rubber tubing mounted on stainless steel rollers especially constructed in our laboratories.

After rubbing, swatches were rinsed in a beaker of tap water for 45 seconds, followed by a 15-second rinse in a second beaker. After the latter rinse, very little radioactive material could be removed from the swatches and a final rinse was performed for one minute under 100° F running tap water.

Depending upon the particular experiment, after the above treatment, wool swatches were either hung up to dry overnight or treated again after excess water was squeezed out using rubber tubing placed over the ends of crucible tongs.

Following treatment and drying, wool swatches were dissolved by placing each in a glass counting vial, adding 1 ml of 2M NaOH, and heating in an oven at 80° C for 1.5 hours. Three reference vials were also prepared in which a wool swatch was dissolved following addition of a known amount of radioactive material.

After cooling, approximately 12 ml of Aquasol-2 LSC cocktail was added to each vial, followed by addition of 0.25 ml of concentrated perchloric acid. The vials were then shaken vigorously, resulting in a clear solution ready for counting.

All measurements with radiotracers were run using only one radiolabeled substance at a time. Thus, for example, in experiments in which both conditioner and detergent deposition were measured for a given treatment series, the series was run twice, once with radiolabeled detergent and once with radiolabeled conditioner.

LIGHT-SCATTERING MEASUREMENTS

The use of a goniophotometer to carry out light-scattering measurements was described in reference 1. In the current work, all goniophotometric measurements were performed using a Murakami GP-1R automatic goniophotometer purchased from Hunter Associates Laboratory, Reston, VA.

The GP-1R, which employs collimated light from a tungsten halogen lamp, has several advantages over the Brice-Phoenix photometer employed in the previous work (1). Among these are the fact that it is a double goniometer instrument so that the sample can be turned to any angle desired with respect to the incident light. In addition, it has a large sample compartment permitting the sensitive stepping motors to run scans from 0° to 75° (or a full 360° if so desired). Finally, the instrument accuracy is quite high, with a specified scan repeatability of ±0.2%, an angle accuracy of ±20′, and a photometric accuracy of ±0.5%.

As in the previous work (1), for all light-scattering experiments, polarizers having directions of polarization perpendicular to the plane of incidence were placed between the light source and the sample and between the sample and the light detector of the goniophotometer. In the current experiments, a Glan-Thompson prism was used in front of the sample, while a sheet polarizer was placed before the light detector.

Figure 1a shows the bottom plate of the GP-1R sample holder used for mounting hair fibers. The diameter of the opening in this plate is 7.3 cm, while the raised plastic ring is 2-mm high and 2-mm thick. In order to accommodate up to 40 hair fibers, the plastic ring contains 40 grooves, 0.635 mm apart, cut at opposite ends of the ring. In all experiments in this work, only one hair fiber was used per scan. These fibers were mounted on the bottom plate under the constant tension supplied by a 2-g alligator clip and held in place by a cover plate secured with two strips of magnetic tape. Figure 1b shows the complete sample holder with a single fiber mounted.

All tress measurements were made by taking 21 hairs from a treated tress, scanning
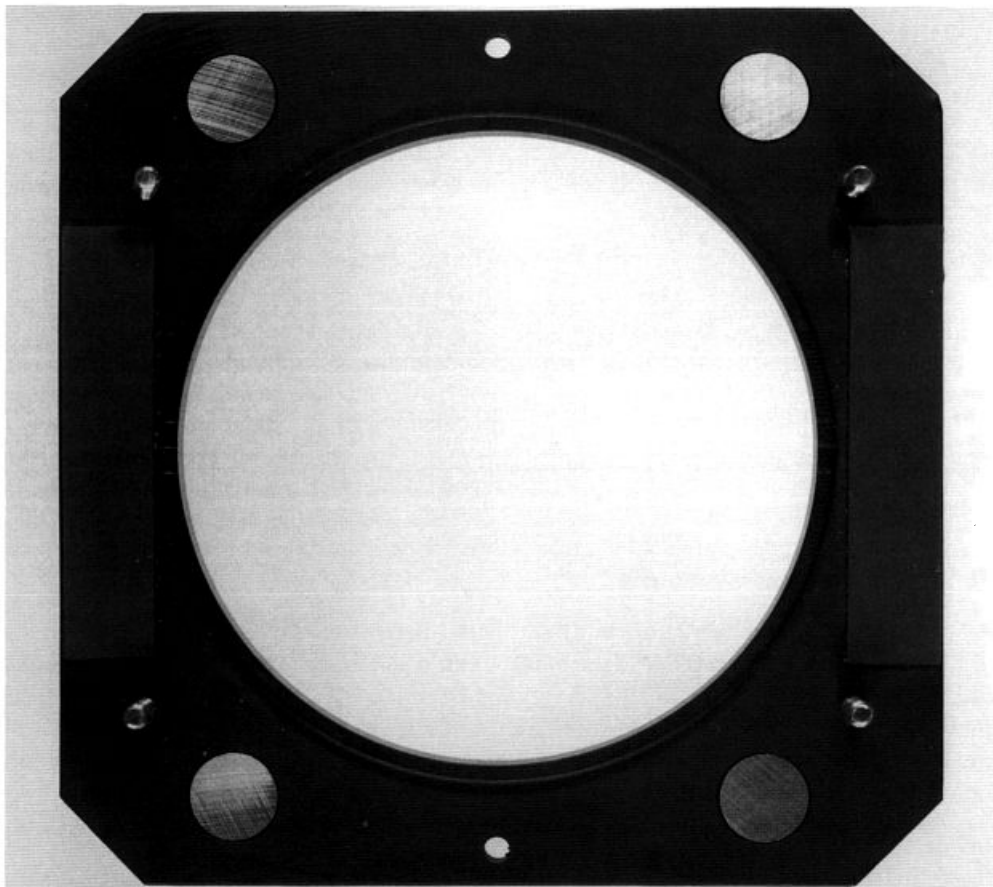
Figure 1a. Photograph of the bottom plate of a GP-1R hair sample holder. Note the four circular magnets set in the bottom plate and the two holes on either side. These are used to mount the sample holder on the vertical mount in the light-scattering instrument.
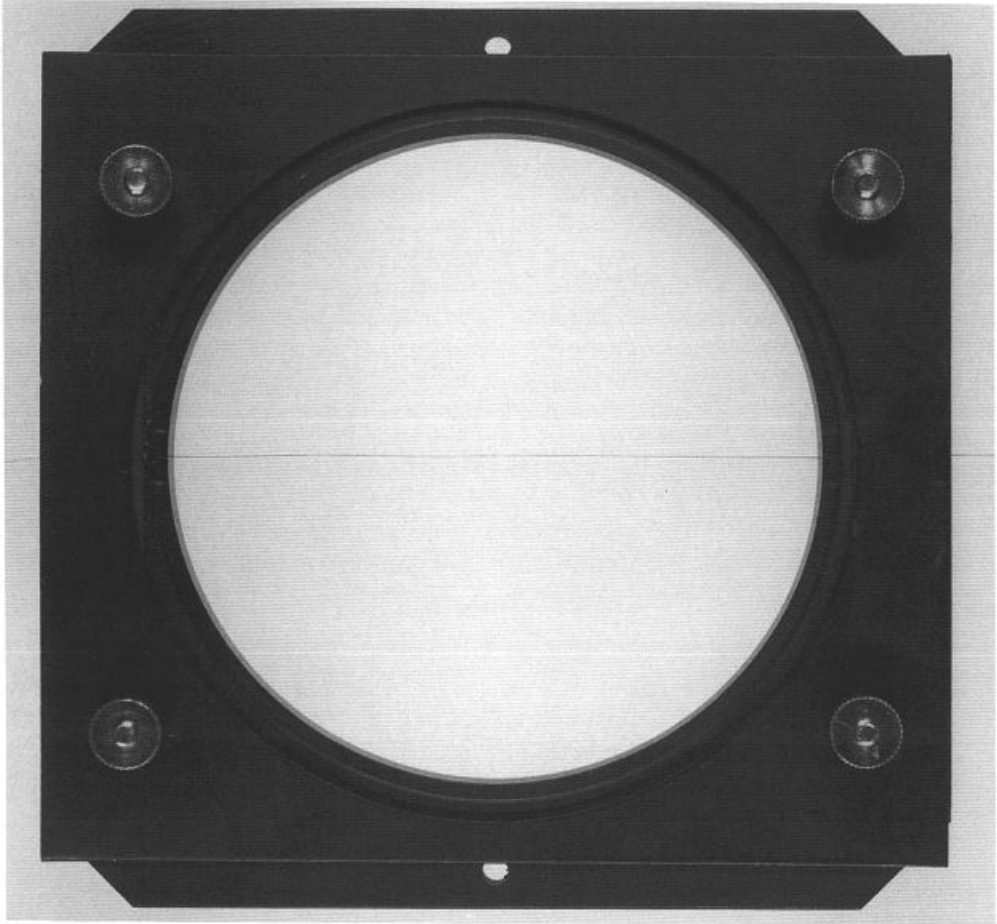
Figure 1b. Photograph of hair sample holder with one hair mounted and top plate in place. Note that the holder is mounted in the GP-1R with the hair fiber in a horizontal position. Also, because of the magnetic tape on the bottom plate, the use of the four fasteners is optional.

them one at a time, as stated above, from $0°$ to $75°$, and averaging the results. The time for a single scan was 75 seconds.

All SAC experiments were run with the hair fibers at an incident angle of $30°$ and oriented so that the direction of incident light was toward the tip of the hair [RER orientation (3)]. All experiments involving commercial conditioner were run at an incident angle of $45°$ in order to compare the results to previous measurements run on the Brice-Phoenix photometer, an instrument on which scans from $0°$ to $75°$ could only be run at $45°$ incidence.

In the Brice-Phoenix experiments, for an RER orientation at $45°$ incidence, reflection from the back walls of hair fibers was found to interfere with the estimate of diffuse scattering at $75°$ (1,3). All the former $45°$ measurements on the Brice-Phoenix instrument, and also the current GP-1R $45°$ measurements, were therefore run with the hair fibers in an REL orientation.

The output from the GP-1R was sent to a Bascom-Turner 3120T electronic recorder (Bascom-Turner Instruments, Norwood, MA) that digitized the 75° scan into 500 points. These points were then sent to an IBM PC computer for processing.

MEASUREMENT OF SHINE

All shine values were calculated from light-scattering parameters, using the previously developed expression (1),

$$L = S/DW(\frac{1}{2})$$ (Eq. 1)

where L is shine, or luster, $W(\frac{1}{2})$ is the width of the spectral peak at half height, and S and D are the integrated specular and diffuse reflectances, respectively. A detailed description of the foregoing terms along with a discussion of hair shine can be found in the previous work (1).

All shine values calculated using equation 1 were averages taken from a minimum of three tress measurements. Since each tress measurement was, in turn, averaged over 21 hairs, each shine value represents an average taken from at least 63 hairs.

STATISTICAL TREATMENT OF DATA

All light-scattering and subjective evaluations performed in the half-head tests were analyzed using a sign test.

All measured shine values of treated tresses and all deposition values from radiotracer experiments were analyzed by means of a one-way analysis of variance (ANOVA) test. In the following tables, measured values of tresses and swatches not significantly different from each other (at a 95% level of confidence) are connected by vertical lines.

RESULTS AND DISCUSSION

STEARALKONIUM CHLORIDE/DETERGENT TRESS EXPERIMENTS

Table I lists the shine values resulting from a large series of SAC/detergent tress experiments. Those tresses treated only with SODS (clean hair) had the highest shine values and thus the greatest shine. Clean tresses treated with SAC, on the other hand, were found to have lowered shine values. This dulling is a result of deposition of SAC particles on the surface of the hair (1,4,5).

An attempt was made to clean SAC-treated tresses with 20% TEALS. Since previous experiments in which clean tresses were washed with TEALS resulted in shine values similar to those obtained with SODS, it was expected that removal of some of the deposited conditioner by the TEALS detergent would cause the measured shine values to increase toward that of clean hair. In Table I it is seen that the shine values did not, in fact, increase upon washing SAC-treated tresses with TEALS but, rather, decreased by a further 42%.

As was the case with interactions of substantive shampoo ingredients (1), such a decrease in shine implies that the anionic TEALS detergent was not very effective in cleaning SAC from the hair surface, but instead interacted with the deposited cationic conditioner

Table I
SAC Tress Experiments[1]

Treatment	No. tresses treated	Shine[2]
SODS	18	1.72 (0.23)
SAC	3	1.15 (0.07)
SAC/TEALS	6	0.67 (0.12)
SAC/SODS	18	1.47 (0.27)
SAC/SDES-2	3	1.53 (0.07)

[1] Shine values connected by a vertical line were not significantly different.
[2] Numbers in parentheses are standard deviations.

to form an insoluble complex that was more dulling to the hair than the original deposited soil.

That such a complex was actually being formed was confirmed by dye-staining experiments, such as were performed in reference 2, in which it was shown that the anionic dye, Red 80, could not stain hair or wool swatches treated with SAC and then washed with TEALS. Since the light-scattering results showed that SAC still remained on the surface of these swatches, these results indicate that the cationic SAC was unavailable for binding to Red 80 because of complexation with lauryl sulfate anion.

The above type of complex formation occurs on the surface of hair because of the insolubility of the SAC:lauryl sulfate interaction product. It was therefore reasoned in reference 2 that changing the chain length of the detergent might render the interaction product more soluble; such a detergent could then effectively clean the SAC from the hair surface rather than form an insoluble complex with it.

This reasoning is shown to be correct by the results in Table I. The shine numbers of SAC-treated tresses washed with the shorter-chain surfactants SODS (C8 and C10 mixture) and SDES-2 were observed to increase in value, becoming almost as great as the value for clean hair. This indicates that these two detergents, unlike TEALS, were effective in removing SAC from the hair surface. We therefore conclude that, as a result of shortening the detergent chain length, SODS and SDES-2 did not form insoluble complexes with SAC, thus leading to improved cleaning of conditioner.

CONDITIONER/DETERGENT RADIOTRACER EXPERIMENTS

In order to test the above light-scattering conclusions, and also to compare the shine values in Table I to relative conditioner/detergent depositions, a series of radiotracer experiments was run measuring deposition on wool swatches after various SAC and detergent treatments.

The results of these measurements are tabulated in Table II. Note that ALS (ammonium lauryl sulfate) rather than TEALS was employed in the measurements in Table II. This was considered to be an acceptable substitute, since both TEALS and ALS produced the same light-scattering results with SAC.

The data in Table II show that, as was concluded above, SDES-2 is superior to lauryl sulfate detergents in cleaning SAC deposits. After washing SAC-treated swatches, ALS removed only 31% of the deposited conditioner vs 62% for SDES-2. In addition, it is

Table II
Deposition From Detergent Cleaning of SAC: Radiotracer Measurements[1,2]

Treatment[3]	SAC per gram wool (mg)	Detergent per gram wool (mg)	Total deposit[4]
1% SAC	6.68 (0.40)	—	6.68 (0.40)
5% ALS	—	1.94 (0.18)	1.94 (0.18)
1% SAC/5% ALS	4.58 (0.72)	4.09 (0.57)	6.73 (0.94)
5% SDES-2	—	1.86 (0.22)	1.86 (0.22)
1% SAC/5% SDES-2	2.52 (0.47)	2.12 (0.33)	2.78 (0.57)

[1] Numbers in parentheses are standard deviations.
[2] Measured values connected by a vertical line were not significantly different.
[3] 0.3 ml of each treatment was applied.
[4] Total deposits for conditioner/detergent washes are calculated by summing conditioner plus detergent deposits minus the detergent deposits on clean wool.

seen that ALS deposition on conditioner-treated swatches was more than twice that on clean substrates. This confirms that lauryl sulfate anions interact with cationic SAC to form an insoluble complex. In the case of SDES-2, binding to clean or conditioner-treated swatches was virtually the same, proving, as was indicated by light scattering, that SDES-2 does not interact with SAC to form insoluble complexes on keratin substrates.

The last column in Table II lists the total amount of deposit found on swatches after different treatments. For SAC-treated swatches washed with ALS, it can be seen that no net cleaning occurred: although some conditioner was removed by ALS, this was replaced by detergent binding to the remaining SAC. In the case of the SDES-2 wash, on the other hand, the net effect was to remove 60% of the original deposit, thus again demonstrating the superiority of SDES-2 in cleaning conditioner.

It should be noted in Table II that the amount of total deposit measured after washing conditioner-treated wool with detergent was adjusted by subtracting that amount of deposit measured after washing clean wool. This does not mean to imply that the subtracted detergent was not part of the conditioner/detergent complex, but was done simply to emphasize the excess of deposit resulting from washing conditioner-treated wool over that resulting from washing clean wool alone.

Table III shows the results of radiotracer experiments in which CTAC was substituted for SAC. The results in this case were similar to those obtained with the latter conditioner. Almost three times as much ALS bound to CTAC-treated swatches as SDES-2,

Table III
Deposition From Detergent Cleaning of CTAC: Radiotracer Measurements[1]

Treatment[2]	CTAC per gram wool (mg)	Detergent per gram wool (mg)
1.7% CTAC	7.13 (0.58)	—
1.7% CTAC/20% ALS	4.25 (0.13)	—
1.7% CTAC/5% ALS	—	4.30 (0.63)
1.7% CTAC/20% SDES-2	2.88 (0.33)	—
1.7% CTAC/5% SDES-2	—	1.47 (0.15)

[1] Numbers in parentheses are standard deviations.
[2] 0.3 ml of each treatment was applied.

indicating, as with SAC, that while CTAC does not interact with SDES-2 to form an insoluble complex, it does form such complexes with ALS on the wool surface. Because of this complex formation, only 40% of deposited CTAC was removed from wool swatches by ALS vs 60% by SDES-2. Total deposits could not be directly calculated because different concentrations of detergent were used in different experiments. It seems clear from the data, however, that, as with SAC, washing CTAC-treated swatches with ALS would result in little or no net cleaning.

SURFACTANT SERIES EXPERIMENTS

The preceding radiotracer experiments confirmed that light scattering can be used to evaluate cleaning of conditioners by surfactants. Using this methodology, the conditioner cleaning efficiency of a series of alkyl ether sulfates having carbon chain lengths of 6, 8, 10, and 12 and degrees of ethoxylation of 1, 3, and 5 was evaluated.

Table IV presents the results for those detergents having a degree of ethoxylation of one. The results indicate that alkyl (1EO) ether sulfates with carbon chain lengths of 6, 8, and 10 are all effective in removing SAC from hair. The same was not found to be true for the C12 detergent, SLES-1EO, which, like TEALS, dulled the hair as a result of complex formation with SAC.

The light-scattering results for the 3EO and 5EO detergents tested were found to be similar to those obtained with the corresponding 1EO species. This indicates that, at least up to 5EO, formation of insoluble detergent:conditioner complexes is determined primarily by the length of the hydrophobic portion of the detergent rather than by the degree of ethoxylation.

CLEANING OF SAC/TEALS COMPLEXES

The preceding material showed that shorter-chain alkyl ether sulfates were superior to conventional, C12-based detergents in cleaning SAC and CTAC, because they do not form the insoluble conditioner:detergent complexes on hair that are formed by the latter surfactants.

The above-mentioned experiments gave no indication, however, of the effectiveness of

Table IV
Shine of SAC/Detergent-Treated Hair[1]

Treatment	Shine[2]
SODS	1.72 (0.23)
SAC/C6-1EO[3]	1.79 (0.22)
SAC/C8-1EO	1.57 (0.09)
SAC/C10-1EO	1.58 (0.16)
SAC/C12-1EO	0.88 (0.07)
SAC/TEALS	0.67 (0.07)

[1] Shine values connected by a vertical line were not significantly different.
[2] Numbers in parentheses are standard deviations.
[3] This is a sodium hexyl ether sulfate substituted with one ethoxy group. The following surfactants in the column are all alkyl (1EO) ether sulfates with the designated carbon chain lengths.

shorter-chain surfactants in cleaning the insoluble SAC:detergent complexes left on hair by the use of conventional detergents.

This was tested by performing light-scattering measurements on tresses that were washed twice with SODS or TEALS following deposition of a TEALS/SAC complex on the surface. In Table V, it is seen that attempting to remove the TEALS/SAC complex with TEALS did not result in significant cleaning, leaving tresses that were still substantially dulled. The SODS treatment, on the other hand, restored most of the original shine, indicating that the complex was effectively cleaned. We conclude, therefore, that detergents such as SODS are superior cleaners, not only of conditioner, but of the insoluble conditioner:detergent complexes left on hair as a result of washing with conventional detergents.

Half-head tests. In addition to tests on single fibers and on tresses, light-scattering results can be obtained from experiments on actual heads of hair. In order to test detergent/conditioner interactions under conditions as close as possible to actual consumer use, therefore, a series of half-head tests was run in which SAC/TEALS and SAC/SODS treatments were compared.

Table VI lists the results of these treatments on ten panelists. A plus sign in the column labeled subjective shine means the SODS-washed side was judged shinier by the evaluators, while a positive value in the delta shine column indicates that the SODS-treated side had the larger measured shine value.

In all ten cases, the SAC/SODS-treated half of the head was found to have the greater measured shine value, while in only one case was the SAC/TEALS-treated side judged to have the greater subjective shine. Application of a simple sign test to these results indicates a difference between the TEALS- and SODS-treated sides at a greater than 99% level of confidence. This confirms that the dulling effects arising from formation of insoluble complexes can be easily observed under conditions similar to actual consumer use.

The one discrepancy above, between instrumental and subjective evaluations, is probably an orientation effect. Shine is observed when an object scatters much more light in a particular direction than in other directions (1). Thus, even if individual hairs in an array are very shiny, the less parallel they are to each other the less they will reflect light in the same direction, resulting in a decrease in perceived shine. The hair in half-head test 6 was quite curly, so it is reasonable to assume it would be more sensitive to orientation effects of this type.

Note that the largest differences in measured shine were observed with permed or

Table V
SAC/TEALS Complex Experiments[1]

Treatment	Shine[2]
SODS	1.72 (0.23)
Complex (SAC/TEALS)	0.67 (0.12)
Complex/TEALS	0.87 (0.11)
Complex/SODS	1.43 (0.23)

[1] Shine values connected by a vertical line were not significantly different.
[2] Numbers in parentheses are standard deviations.

Table VI
SAC Half-Head Tests. (SODS vs TEALS)

Test no.	Subjective[1] shine	Delta[2] shine
1[3]	+	0.26
2	+	0.12
3	+	0.11
4	+	0.38
5	+	0.50
6	−	0.44
7[4]	+	0.80
8[5]	+	0.38
9	+	0.63
10[4]	+	0.80

[1] A positive sign means SODS-treated side judged shinier.
[2] This is the difference between shine values measured for SODS and TEALS-treated sides. A positive value means SODS side had greater shine.
[3] Tests 1–3 were performed on the same woman.
[4] These women had permed hair.
[5] Tests 8 and 9 were performed on same woman before and after application of a hair-straightening treatment.

straightened hair. This is not surprising since chemically treated hair has a greater number of negative charges on the surface and would be expected to bind more cationic conditioner. This is confirmed by the observation from radiotracer experiments that permed hair binds 2.3 times more SAC than virgin hair (6).

Cleaning of commercial conditioners. The preceding experiments dealt for the most part with SAC, a conditioner active found in many commercial products. Experiments were also performed with conditioner A, a commercial conditioner containing SAC and ceteth-2, in order to determine whether the results reported for SAC would also be observed with commercial products.

Tresses treated with conditioner A and then washed with TEALS were found to exhibit much less dulling than was observed when washing SAC-treated tresses. This is probably the result of solubilization of the SAC by the ceteth-2 oil. In order to increase the sensitivity of the experiments, therefore, measurements were made using permed tresses which, as was noted in the preceding section, adsorb more conditioner than does virgin hair.

Table VII tabulates the light-scattering results from a typical permed hair experiment. In this case it is seen that, as was observed for SAC-treated hair, washing conditioner A-treated hair with TEALS resulted in duller tresses than those washed with the shorter-chain surfactants comprising SODS. This was confirmed by panelists who subjectively evaluated tresses according to the methods described in reference 1.

These results indicate that, although the dulling effect is smaller, formation of insoluble complexes between TEALS and SAC still occurs with commercial conditioners.

Note that the shine values in Table VII were obtained at 45° incidence and thus cannot be compared directly with the 30° incidence shine values listed in the previous tables. The reason for this is that specular reflection increases with increasing angle of incidence (Fresnel's equations, reference 3).

Table VII
Commercial Conditioner Treatments of Permed Hair[1,2]

Treatment	Shine[3]
SODS	2.57 (0.28)
Conditioner A[4]/SODS	2.58 (0.06)
Conditioner A/TEALS	2.08 (0.05)

[1] Shine values connected by a vertical line were not significantly different.
[2] The angle of incidence in these experiments was 45°.
[3] Numbers in parentheses are standard deviations.
[4] This is a commercial conditioner containing SAC and ceteth-2.

Commercial conditioner half-head tests. A series of half-head tests was run with conditioner A to determine if the treatment differences noted for tresses could be observed on heads of permed hair. In these experiments, following conditioner treatment, one side of the head was washed with TEALS while the other side was washed with SODS.

Overall, a total of 26 half-head tests evaluating cleaning of conditioner A were run. The most consistent subjective differences found in these tests were associated with shine and the existence of a coated feel to the hair on one side of the head.

In 23 of the 26 half-head tests, the evaluators chose the SODS-treated half of the head as being the cleaner side. In the three cases where this was not true, the TEALS side may have been chosen because of the previously mentioned orientation effects. Even discounting this possibility, however, statistical analysis indicates a difference between the TEALS and SODS sides at a greater than 99% level of confidence.

The greater shine of the SODS-washed hair was also supported by the light-scattering results. Table VIII lists those half-head tests for which instrumental measurements were performed. For 10 of the 11 measurements, the SODS side had the higher shine value, while for the eleventh test, the shine values were essentially equal.

Table VIII
Commercial Conditioner (Conditioner A) Half-Head Tests.[1] (SODS vs TEALS)

Test no.	Subjective[2] shine	Delta[3] shine
11	+	0.74
11[4]	+	0.50
12[4]	−	0.74
13	+	0.15
14	+	0.37
14[4]	+	0.88
15[4]	+	0.61
16[4]	+	0.26
17[4]	+	0.23
18[4]	+	−0.07
19[4]	+	0.23

[1] The angle of incidence in these experiments was 45°. All subjects had permed hair.
[2] A positive sign means SODS-treated side judged shinier.
[3] This is the difference between shine values measured for SODS and TEALS-treated sides. A positive value means SODS side had greater shine.
[4] Conditioner was last treatment prior to viewing and hair sampling.

These results confirm that for commercial products as well as for SAC, the superior cleaning of conditioners by shorter-chain surfactants such as those found in SODS can be observed under conditions similar to actual consumer use.

Commercial conditioner/detergent radiotracer experiments. As was done with conditioner actives, radiotracer experiments were run with conditioner A doped with [^{14}C]SACL in order to confirm the light-scattering results and also to obtain an idea of relative amounts of deposition.

The results of these experiments are tabulated in Tables IX and X. Unlike the case with conditioner actives, it is seen that both ALS and SODS are equally effective in cleaning SAC deposited from conditioner A. In addition, the amount of SAC left on the hair is approximately the same after one or two treatment cycles, indicating that, at least in this limited case, SAC did not build up on the surface of the swatch.

Interaction between ALS and the SAC in conditioner A still occurs, however. This is indicated by the fact that binding of ALS to conditioner A-treated swatches was more than three times greater than binding to clean swatches. Such deposition, replacing as it does, cleaned conditioner, greatly reduces the net cleaning by ALS. This situation is made worse by buildup of ALS with repeated treatment: after three conditioner/wash cycles, ALS deposition was 28% greater than after one cycle.

The increased binding of ALS to conditioner-treated swatches was not exhibited by SDES-3. In Table IX it is seen that the same amount of SDES-3 was deposited on clean swatches as on conditioner A-treated swatches, indicating, as was seen in the light-scattering experiments, that SDES-3 does not interact with conditioner A to form insoluble complexes on keratin surfaces.

Table IX also lists the results of experiments in which the conditioner A/SDES-3 treatment cycle was applied to swatches three times. No increase in SDES-3 deposition

Table IX
Deposition From Detergent Cleaning of Commercial Conditioner: Radiotracer Measurements[1,2]

Treatment	SAC per gram wool (mg)	Detergent per gram wool (mg)	No. cycles
Conditioner A[3]	4.27 (0.59)	—	1
Cond. A/5% SODS[3]	1.83 (0.67)	—	1
Cond. A/5% ALS[3]	1.67 (0.24)	—	1
Cond. A/5% SODS[3]	2.05 (0.56)	—	2
Cond. A/5% ALS[3]	2.03 (0.55)	—	2
5% ALS[4]	—	1.18 (0.08)	1
Cond. A/5% ALS[4]	—	3.57 (0.13)	1
Cond. A/5% ALS[4]	—	3.79 (0.18)	2
Cond. A/5% ALS[4]	—	4.58 (0.19)	3
5% SDES-3[4]	—	1.11 (0.19)	1
Cond. A/5% SDES-3[4]	—	1.08 (0.08)	1
Cond. A/5% SDES-3[4]	—	1.17 (0.30)	2
Cond. A/5% SDES-3[4]	—	0.98 (0.31)	3

[1] Numbers in parentheses are standard deviations.
[2] Measured values connected by a vertical line were not significantly different.
[3] 0.3 ml of each treatment was applied.
[4] 0.15 ml of each treatment was applied.

Table X
Deposition From Shampoo Cleaning of Commercial Conditioner: Radiotracer Measurements[1]

Treatment[2]	SAC per gram wool (mg)	TEALS per gram wool (mg)	Total deposit[3]
Conditioner A	3.17 (0.19)	—	3.17 (0.19)
Shampoo B[4]	—	1.37 (0.10)	1.37 (0.10)
Cond. A/Shampoo B	1.66 (0.25)	3.09 (0.52)	3.28 (0.59)

[1] Numbers in parentheses are standard deviations.
[2] 0.15 ml of each treatment was applied.
[3] Total deposit for the conditioner/shampoo treatment was calculated by summing the SAC and TEALS and subtracting the TEALS deposits on clean wool.
[4] This is a TEALS-containing commercial shampoo.

was observed with repeated treatment, indicating that, unlike ALS, SDES-3 does not build up on conditioner-treated swatches.

Table X shows the results of experiments in which shampoo B, a TEALS-containing commercial shampoo, was used to wash conditioner A-treated swatches. As was the case with SAC and TEALS alone, the shampoo exhibited increased deposition in the presence of conditioner as a result of SAC/TEALS complex formation. Because of this increased deposition, no net cleaning was observed: the total deposits before and after shampooing were comparable. This indicates that for fully formulated commercial products as well as for the active ingredients, formation of insoluble complexes between cationic conditioners and anionic detergents can occur on hair.

CONCLUSIONS

In this paper, light-scattering measurements, supplemented by radiotracer techniques, were used to demonstrate the formation on hair surfaces of dulling, insoluble complexes between common conditioner actives and the lauryl and laureth sulfate detergents used in virtually all commercial shampoos.

Washing deposited conditioner active with the above C12 detergents was shown to result in little net cleaning as a result of buildup of both conditioner and detergent on the hair surface. Detergents with hydrophobic chain lengths less than 12 were shown to be superior to laureth sulfates in cleaning conditioner because of the absence of complex formation and also because of their ability to solubilize any previously formed complex.

In the case of commercial conditioners, buildup was observed only from C12 detergents, rather than from detergent and conditioner. This led to less dulling; however, enough increased deposition from detergent was observed to occur, to again lead to little net cleaning by commercial shampoos.

The above-documented buildup from conditioning, shampoo cycles could be a contributing factor to the common consumer belief that the cleaning effectiveness of any particular shampoo decreases over time. A better understanding of the possible causes for decreases in cleaning with repeated use, such as the interactions documented in the present work, could result in products that would command more consumer loyalty.

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