

Assessment of the substantivity of cationic quaternary compounds to hair by potentiometric titration using the surfactant electrode

NGHI VAN NGUYEN, DAVID W. CANNELL,
ROGER A. MATHEWS, and HANS H. Y. OEI, *Redken
Laboratories Inc., Research and Development Department, 6625 Variel
Avenue, Canoga Park, CA 91303.*

Received February 7, 1992.

Synopsis

A new method to measure the sorption of cationic quaternary compounds by hair is reported. The method employs the potentiometric titration of cationic compounds, using a surfactant electrode as an endpoint indicator. Cationic uptake was determined from the difference of the cationic content in the solutions before and after the treatment of hair. By this method, the substantivity to bleached hair of mono- and poly-functional quaternary ammonium conditioning agents, as well as animal and botanical quaternary ammonium proteins, was measured as laurdimonium hydrolyzed wheat protein > quaternium-26 > stearalkonium chloride > cocodimonium hydrolyzed keratin protein. The results are consistent with previously published accounts: cationic uptake of quaternary compounds increases with increased solution concentration, treatment time, temperature, and hair damage.

INTRODUCTION

Quaternary ammonium compounds have been widely used as hair conditioning agents in cosmetics. These compounds encompass cationic surfactants, cationic polyelectrolytes (polyquaternary polymers, copolymers), and cationic quaternary derivatives of hydrolyzed proteins (animal, botanical). Deposition (substantivity) of these cationic compounds on hair can produce effects on fiber friction (i.e., wet and dry combing), stiffness, gloss, anti-static qualities, and strength (1). The substantivity of these cationic species to hair has been measured by various methods. These methods can be complicated, time-consuming, expensive, and non-quantitative.

Light and electron microscopy have been used to visually evaluate the cosmetic effect of substantive proteins (2). Another non-quantitative method is the Rubine dye test in which the cationic uptake by hair is proportional to the intensity of the color developed after the reaction of an anionic dye and the adsorbed cationic compound (3).

Some sophisticated means for the qualitative evaluation of the deposition of polymers and surfactants on the surface of hair include the use of the wetting force measurement

of individual fibers (4), wettability scanning and microfluorometry (5), and electron spectroscopy for chemical analysis (6). These methods require expensive instrumentations and expert acquisition and interpretation of the data.

One of the most powerful methods to measure the substantivity of quaternary compounds to hair is the application of radiotracer techniques (7–9). Being quantitative and accurate, this method is time-consuming and requires synthesis of radio-tagged starting materials.

Spectrophotometric methods have also been widely used to analyze the substantivity of conditioning agents to hair. One method involves the absorbance measurement of the quaternary ammonium surfactant–Orange II dye complex (10,11). This procedure requires elaborate sample preparations.

Recently, colloid titration (12) was shown to be a useful method to quantify the sorption of cationic polymer to bleached hair (13). The technique is based on a direct neutralization reaction between cationic species and potassium polyvinylsulfate. The color change of the *o*-toluidine blue indicator indicates the end point of the neutralization process.

Another way to follow the neutralization process is by means of potentiometric titration. In this method, the positive potential reading of the cationic solution decreases as the cationic compound is allowed to react with the anionic standard solution. The complete 1:1 ion pair interaction is determined with the surfactant electrode as an endpoint indicator (14,15). This technique is simple, fast, and reproducible. Application of the potentiometric titration with a surfactant electrode as an analytical tool in the cosmetic industry has not been reported in the literature. Only recently, Oei *et al.* applied this method to quantitatively analyze simple cationic surfactants in a commercial shampoo (16).

The present investigation demonstrates the feasibility of the potentiometric titration of various mono- and polyfunctional quaternary ammonium conditioning agents as well as animal and botanical quaternary ammonium proteins. It also demonstrates the application of this simple method in quantitative measurement of the substantivity of these cationic quaternary compounds to hair under various experimental conditions.

EXPERIMENTAL

MATERIALS

The cationic quaternary ammonium compounds tested in this investigation include cationic conditioners, cationic cellulosic polymer, cationic wheat protein, and cationic keratin protein (Table I). All compounds are commercial grade and used as received. Only stearylalkonium chloride is not soluble in water at room temperature; however, upon warming (40°C), it remains water-soluble under the conditions of the test.

METHOD FOR POTENTIOMETRIC TITRATION

The titration procedure was adopted from Oei *et al.* (16): a solution containing a measured amount of cationic compound, 0.6 ml of 0.01 N HCl, 2 ml of 1% solution

Table I
General Information of Tested Quaternary Compounds

Material	CTFA adopted name	% Solid	pH	Source
Celquat L-200	Polyquaternium-4	90-95	5-6	Nat'l Starch ¹
Carsoquat SDQ-85	Stearylalkonium Chloride	85-90	5-6	Lonza ²
Ceraphyl 65	Quaternium-26	53-63	5-6	Van Dyk ³
Hydrotriticum QL	Laurdimonium hydrolyzed wheat protein	28-32	4-6	Croda ⁴
Croquat WKP	Cocodimonium hydrolyzed keratin protein	28-32	4-5	Croda ⁴

¹ National Starch and Chemical Company, Specialty Polymer, FINDERNE Avenue, Bridgewater, NJ 08807.

² Lonza, 17-17 Rt 208, Fair Lawn, NJ 07410.

³ Van Dyk, Main and William Sts., Belleville, NJ 07109.

⁴ Croda Inc., 183 Madison Avenue, New York, NY 10016.

of octoxynol-9 in water (Rohm & Haas), and distilled water (total volume 100 ml) was titrated by a Brinkman Potentiograph E536 connected to a Dosimat E535 that dispenses a standard 0.01 M sodium dodecylsulfate (SDS; E. Merck) at a rate of 3.5 ml/minute. The change in the potential was monitored by a surfactant electrode, Model 93-42, obtained from Orion Research. From the potentiogram, the endpoint was determined as the point of steepest slope by a tangent template. All solutions were titrated at a pH of 2-3.

PREPARATION OF CALIBRATION CURVES

Solutions containing 10, 20, 40, and 80 mg (corrected for average percent solid) of cationic compound were prepared in triplicate and titrated with 0.01 M SDS solution as described above. It was not necessary to correct for a blank since the titration does not yield any endpoint (no neutralization process occurs). The calibration curves were obtained by plotting the weight (mg) of cationic compounds vs the volume (ml) of standard SDS solution used in the titration.

SUBSTANTIVITY STUDY

Unless otherwise noted, the procedure to measure the substantivity of quaternary compounds is as follows: 0.1 g of bleached hair was added to a 40-ml solution of quaternary compound that was then placed in a 35°C shaker bath for 30 minutes. At the end of the treatment time, the solution was decanted and the hair was rinsed (3×20 ml) with distilled water. The combined solution (100 ml) was titrated with 0.01 M SDS solution as described above. An untreated sample (without hair) was subjected to the same conditions. All experiments were performed in triplicate. The average of three determinations was obtained, and the quantity of the quaternary compound in the titrated solutions was calculated from the appropriate calibration curve. The calculated difference in the amount of cationic compound present in the untreated and treated solutions represents the cationic uptake by the hair sample.

The effect of the rinse on the desorption of cationic compounds from the hair is not

definitive. The amount of the quaternary compound found in the rinse (about 1% of the adsorbed quantity) may not result from the desorption, but instead from the residual solution adhering to the hair tress.

HAIR SAMPLES AND CHEMICAL TREATMENTS

Light brown, normal virgin (NV) quality European hair (DeMeo Brothers, New York) was used as received throughout the study. Virgin hair tresses were bleached with Levitation Bleach™ powder (Redken Laboratories, Inc.) mixed with 9% hydrogen peroxide. The tresses were saturated with bleach, covered with plastic film, and incubated at 35°C for 45 minutes. The hair tresses were then rinsed under a stream of distilled water for five minutes and air dried (B1×). The same procedure was repeated on the B1× hair to obtain two-time bleached hair (B2×). The permanent waving procedure utilized a commercial alkaline permanent wave, Perm Art™ (Redken Laboratories, Inc.). Reduction of hair samples was accomplished by saturating hair with a solution containing 9% thioglycolic acid (pH 9.5) at 30°C for 15 minutes. The tresses were then rinsed under a stream of distilled water for three minutes and blotted dry. These reduced tresses were saturated with neutralizing solution (2% hydrogen peroxide) for five minutes, rinsed with distilled water for five minutes, and air dried (P1×). The same procedure was repeated on the P1× hair to obtain two-time permed hair (P2×). Tinted hair (T) was obtained by using a commercial cream color (Deco Color™ 6RU, Redken Laboratories, Inc.) mixed with 6% hydrogen peroxide. Hair tresses were saturated with the color at 38°C for 45 minutes, then rinsed under a stream of distilled water for five minutes and air dried.

AMINO ACID ANALYSIS

Hair samples were hydrolyzed in sealed evacuated tubes with 6N HCl at 110°C for 48 h. The hydrolysates were then analyzed on a Beckman 121M or 6300 amino acid analyzer following a previously reported procedure (17).

RESULTS AND DISCUSSION

To illustrate the versatility and the efficiency of the new method, a variety of quaternary compounds were tested (Table I). Since the present procedure is an aqueous titration, the quaternary compounds should be water-soluble. However, water-insoluble or dispersible compounds can also be used if they are solubilized in mixed solvent systems such as water-alcohol mixtures.

In the present study, a 0.01 M SDS solution was used as the titrant because it is a designated standard for the Orion surfactant electrode. Also, in the potentiometric titration of quaternary ammonium compounds, one of the main criteria for a successful quantitative analysis is the presence of a sufficiently large potential decrease at the endpoint. The titration curves should display a pronounced inflection at the endpoint such that the point of steepest slope can be obtained accurately and reproducibly. Typical potentiometric titration curves obtained for the tested cationic compounds are shown in Figure 1. All of the curves in Figure 1 show a suitable potential decrease and

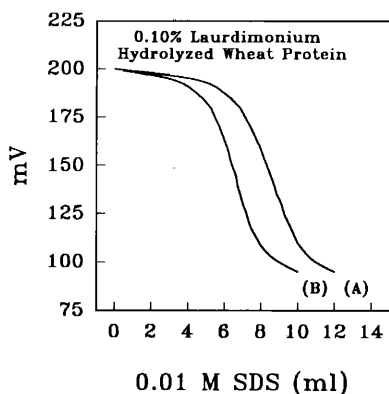
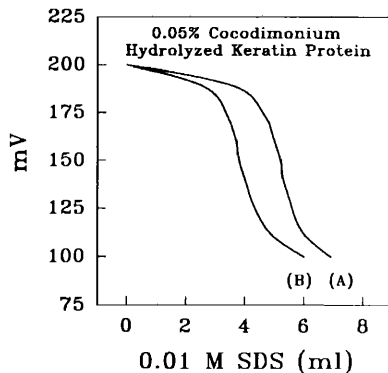
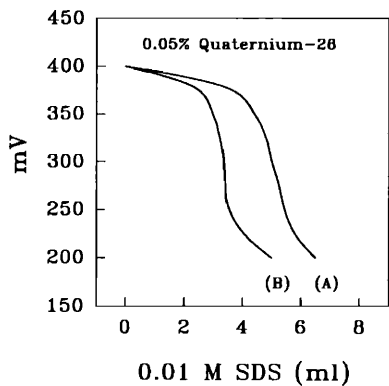
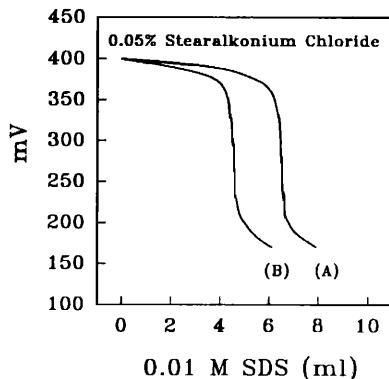
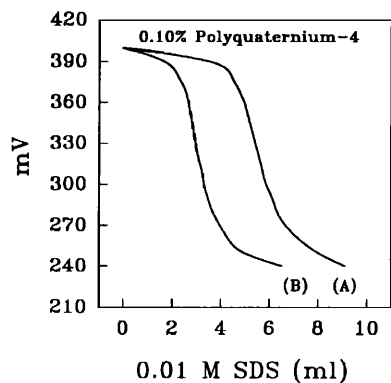


Figure 1. Typical potentiometric titration curves of polyquaternium-4, stearalkonium chloride, quaternium-26, cocodimonium hydrolyzed keratin protein, and laurdimonium hydrolyzed wheat protein solutions before (A) and after (B) treatment with bleached hair.

a well-defined endpoint. It is therefore possible to potentiometrically titrate various cationic quaternary compounds, ranging from simple surfactants to macromolecules such as polymers and proteins.

Figure 1 also demonstrates the application of the potentiometric titration to directly measure the amount of quaternary compounds adsorbed to bleached hair. As shown in Figure 1, the titration curves of the treated samples, compared to the untreated ones, show a decrease in the volume of SDS solution needed to reach the endpoint. The difference reflects the amount of cationic compounds adsorbed to hair. The results illustrate the feasibility of using this simple titration method to evaluate the substantivity of various cationic compounds to hair.

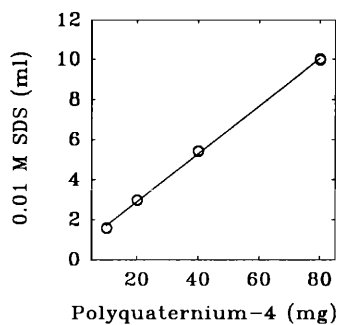
In order to quantitate substantivity to hair, calibration curves for each cationic compound tested (Table I) were generated. As illustrated in Figure 2, the calibration curves show linearity (correlation coefficient = 0.99) over the range tested. The replication of the experimental points also indicates the reproducibility of the titration of various cationic quaternary ammonium compounds by means of the potentiometric titration by a surfactant electrode. Assessment of the substantivity of cationic compounds under various conditions by this convenient titration method was carried out, and the results are shown below. Again, confidence in results is reflected by the low relative standard deviation (averaging about 2%) of the triplicate experiments throughout the study.

Figure 3 shows the effect of the solution concentration of polyquaternium-4, laurdimonium hydrolyzed wheat protein, and quaternium-26 on the cationic uptake by bleached hair. Tests were performed using 0.05, 0.10, 0.20% (w/v) solutions of the quaternary compound. The results indicate that the cationic uptake of bleached hair increases with the concentration of the quaternary solution. The rate of increase is greatest with polyquaternium-4. However, laurdimonium hydrolyzed wheat protein has the highest cationic uptake at the lowest concentration. Similar concentration effects on the substantivity of the cationic compounds has been demonstrated (8,13,18).

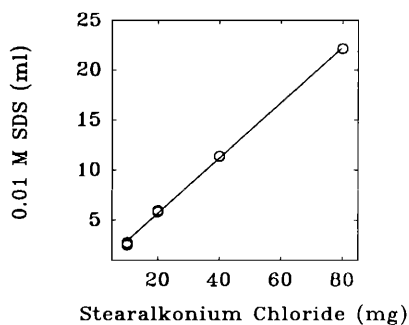
The effect of treatment time on quaternary ammonium compound sorption is shown in Figure 4. Bleached hair was treated for 5, 15, and 30 minutes at 35°C with 0.10%, 0.05%, and 0.05% solutions of polyquaternium-4, cocodimonium hydrolyzed keratin protein, and quaternium-26, respectively. Figure 4 shows that increasing the treatment time results in increasing sorption of cationic compounds by hair. By means of colloid titration and radiotracer techniques, the same results were obtained with other quaternary polymers (9,13). It has been suggested that this increased uptake is the result of the ability of the cationic compounds to penetrate or diffuse into the hair fiber.

The sorption of quaternium-26, stealkonium chloride, and laurdimonium hydrolyzed wheat protein was also determined at different temperatures. The experiments were performed at 23°C and 35°C for ten minutes with 0.05% (w/v) solutions of quaternium-26 and stealkonium chloride and a 0.10% (w/v) solution of laurdimonium hydrolyzed wheat protein. The results (Figure 5) show an increase in cationic uptake of all compounds at higher temperature. The fact that the cationic sorption increases with increased temperature was also found in other studies and thought to be due to the higher penetration rate of the cationic compounds into the hair fiber (11).

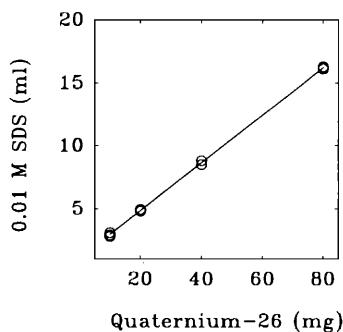
The effect of hair damage on cationic uptake by hair is shown in Figure 6. Qualitatively, hair damage is reflected by the chemical process applied to hair such as perm, tint, or



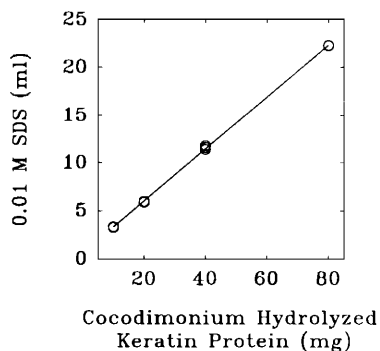
Intercept = 0.53
Slope = 0.12
 $r^2 = 0.99$



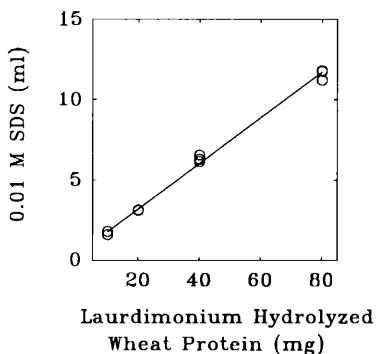
Intercept = 0.15
Slope = 0.28
 $r^2 = 0.99$



Intercept = 1.08
Slope = 0.19
 $r^2 = 0.99$



Intercept = 0.61
Slope = 0.27
 $r^2 = 0.99$



Intercept = 0.36
Slope = 0.14
 $r^2 = 0.99$

Figure 2. Calibration curves showing the linearity of polyquaternium-4, stearalkonium chloride, quaternium-26, cocodimonium hydrolyzed keratin protein, and laurdimonium hydrolyzed wheat protein titrated with SDS.

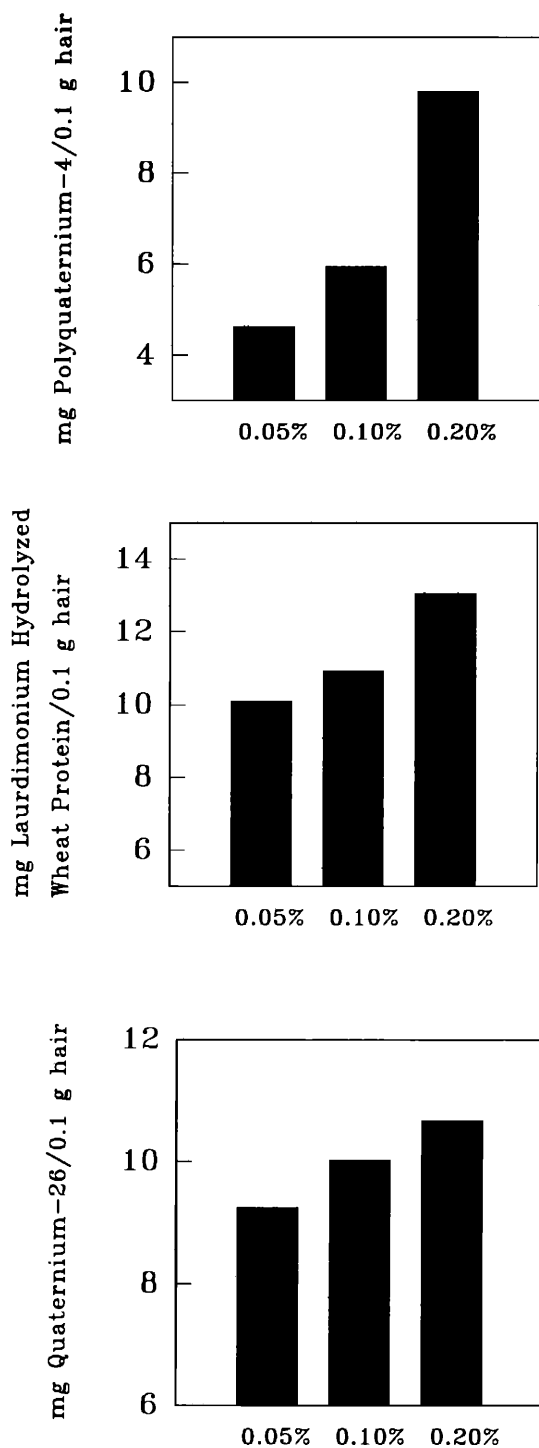


Figure 3. The effect of solution concentration of polyquaternium-4, laurdimonium hydrolyzed wheat protein, and quaternium-26 on cationic uptake by bleached hair.

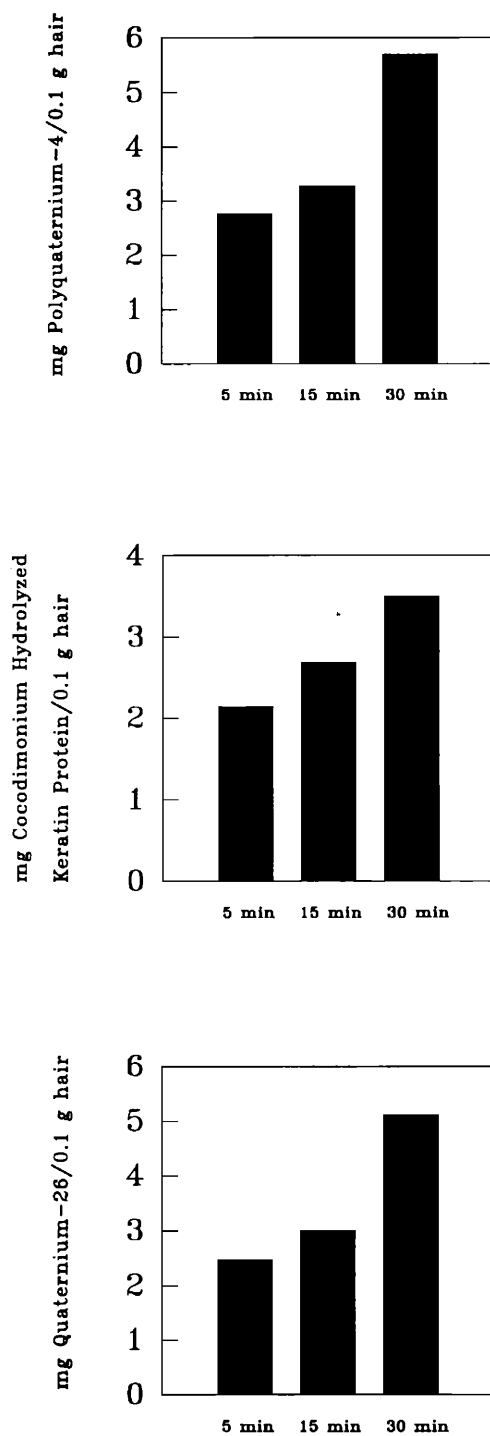


Figure 4. The effect of treatment time on polyquaternium-4, cocodimonium hydrolyzed keratin protein, and quaternium-26 sorption by bleached hair.

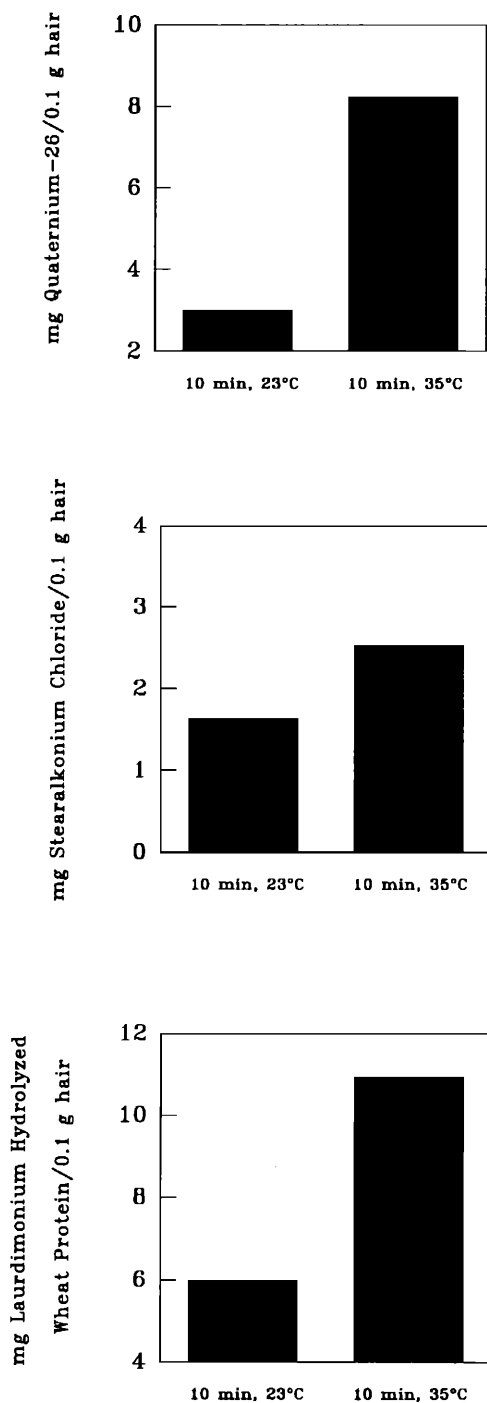


Figure 5. The effect of temperature on the sorption of quaternium-26, stearylalkonium chloride, and laurdimonium hydrolyzed wheat protein by bleached hair.

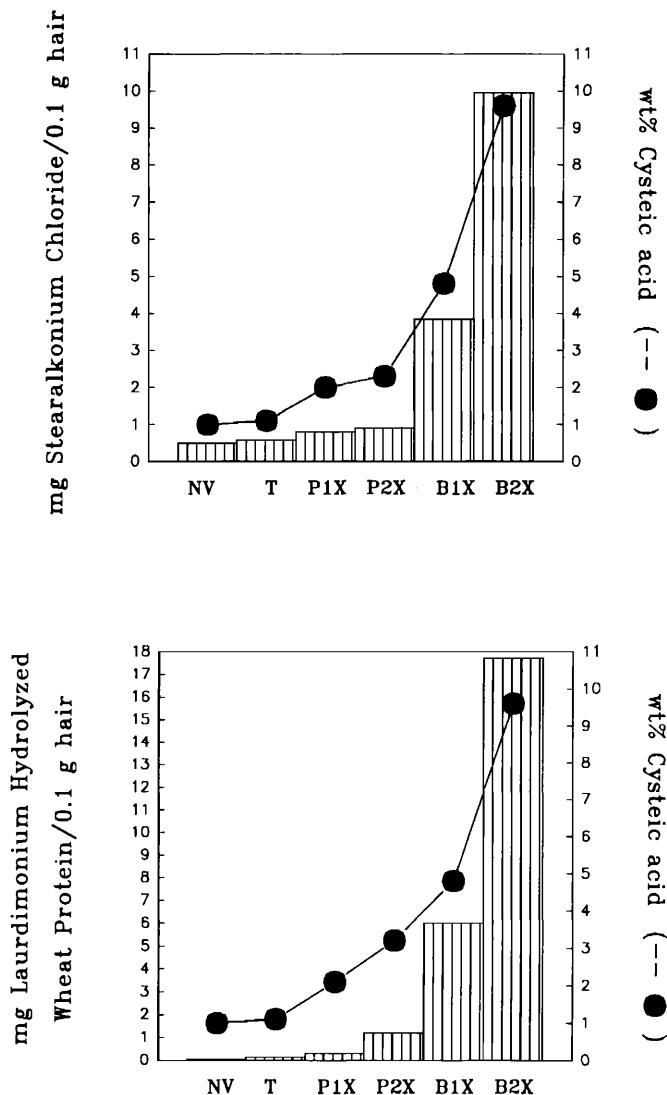


Figure 6. The effect of condition and cysteine acid content of hair on stearalkonium chloride and laurdimonium hydrolyzed wheat protein sorption (NV = normal virgin hair; T = tinted hair; P1X, 2X = one-time, two-time permed hair; B1X, 2X = one-time, two-time bleached hair).

bleach. Other indications of hair damage may be obtained from the measurement of cysteine acid content which, in a study of the effects of reactive chemical processes on hair, was shown to be pronounced at the cuticle layer of the hair (17). Two examples are displayed in Figure 6: uptake of stearalkonium chloride and laurdimonium hydrolyzed wheat protein at various hair conditions. As the hair became more damaged (increase of wt% cysteine acid), the amount of cationic compounds adsorbed to hair increased. This phenomenon has been well recognized (11,13,19). By the same token, hair with oxidative damage adsorbs cationic compounds more readily than hair with reductive damage. The results suggest a phenomenon in which the cationic ammonium compounds are

attracted by the anionic sulfonate group of the cysteic acid at the outer layer of the hair fiber.

Relative comparison of the substantivity of the cationic compounds can also be made on the basis of their equivalent weight. Quaternary molecules having higher equivalent weight exhibit better substantivity. In the present study, an apparent equivalent weight of the compounds tested can be readily calculated from the calibration curves (Figure 2) by the following equation:

$$\text{Equiv wt (mg/mequiv)} = \frac{1}{\text{slope} \times N_{\text{SDS}}}$$

where

slope = slope of the appropriate calibration curve (ml_{SDS}/mg cationic compound)

N_{SDS} = normality of SDS titrant (0.01 mequiv/ml)

Table II shows the calculated equivalent weights obtained from the potentiometric titration method under the tested conditions. These values may not represent the "true" equivalent weight of the cationic compounds since their titration is based on the assumption of a complete 1:1 ion pair interaction. For example, the calculated value for stealkonium chloride is 357 mg/mequiv whereas the theoretical value is 423 mg/mequiv. Among other factors, titratable impurities in the commercial grade samples are possibly accountable for such a discrepancy.

Table II also shows the quantitative uptake of the quaternary compounds by bleached hair that was treated at 35°C for 30 minutes with a 0.05% solution of the cationic compound. The calculated equivalent weights display an order of stealkonium chloride ≈ cocodimonium hydrolyzed keratin protein < quaternium-26 < laurdimonium hydrolyzed wheat protein < polyquaternium-4. This trend is similar to the order of the substantivity of these compounds to hair, i.e., stealkonium chloride ≈ cocodimonium hydrolyzed keratin protein < quaternium-26 < laurdimonium hydrolyzed wheat protein. Polyquaternium-4, having the highest equivalent weight, displays the lowest substantivity. This anomaly is not well understood. However, the high rate of increase in substantivity of polyquaternium-4 at higher concentration and longer treatment time is noted (Figures 3,4). Thus, even though a standardized method for the study of the

Table II
Comparison of the Calculated Equivalent Weight and the Substantivity of Tested Compounds

Material	Calculated equivalent weight (mg/mequiv)	Substantivity using 0.05% solution (mg/0.1 g hair)
Stealkonium chloride	357	8.65
Cocodimonium hydrolyzed keratin protein	370	8.43
Quaternium-26	526	9.25
Laurdimonium hydrolyzed wheat protein	714	10.09
Polyquaternium-4	833	4.62

substantivity of cationic compounds has not been developed, based on the present experimental conditions laurdimonium hydrolyzed wheat protein exhibits the greatest substantivity, followed by quaternium-26, stearammonium chloride, and cocodimonium hydrolyzed keratin protein.

The bulk of the present study was performed on aqueous solutions of the quaternary ammonium compounds used neat. Interference by other components (cationic, anionic, or amphoteric) present in formulated products have not yet been fully assessed. However, a potentiometric titration curve of a commercial aqueous-based protein hair conditioner (CAT™, Redken Laboratories, Inc.) shows no apparent interference encountered in titration of a quaternized protein in a complex formulation. The result from this

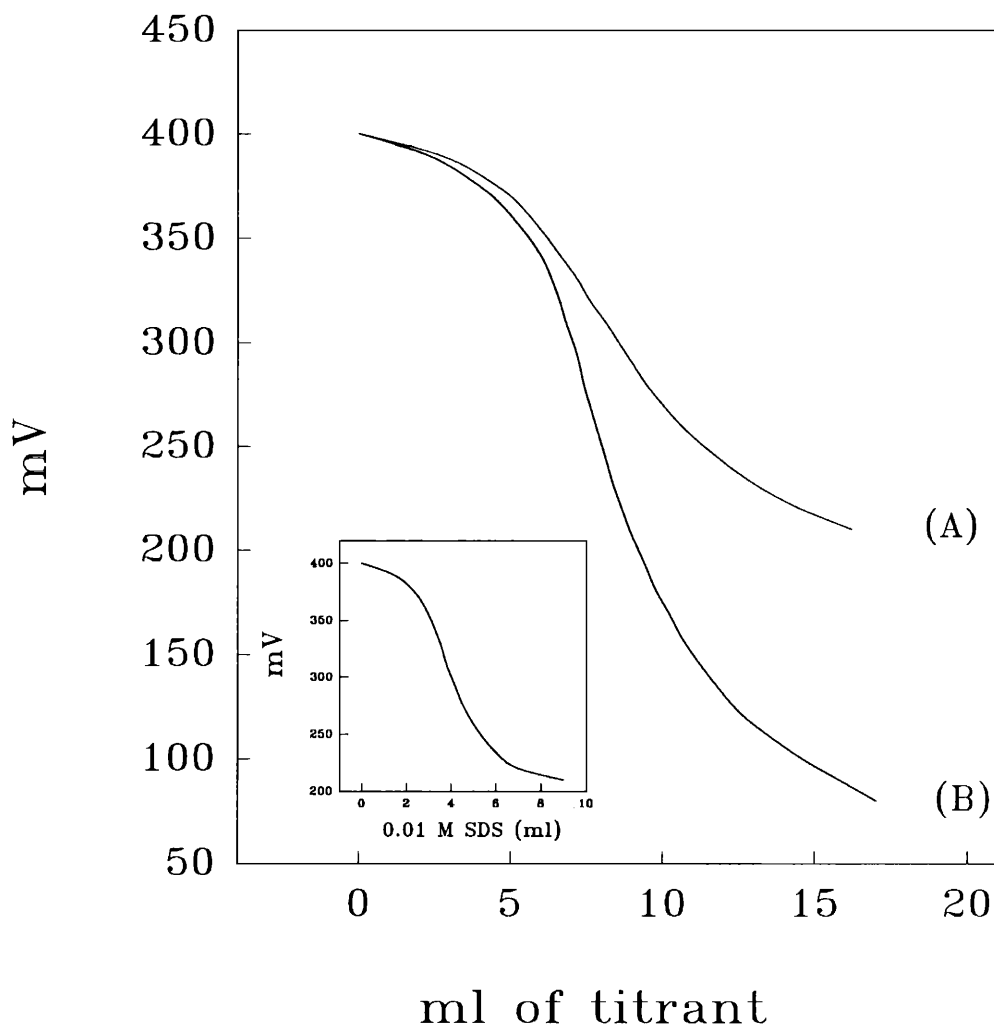


Figure 7. Potentiometric titration curves of a commercial protein conditioner with 0.01 M SDS as titrant (A) and 0.01 M STPB as titrant (B). The titration curve of the neat botanical quaternized protein used in this conditioner is also shown (inset).

titration indicates, with 5% error, the actual level of the cationic protein present in this hair conditioner. Also, Figure 7 illustrates the high potential jump at the endpoint of the titration curve of this conditioner. This curve is similar to the one, shown in the inset, of the quaternized protein, a main ingredient in the tested conditioner. Moreover, it is noteworthy that the potential jump of this titration curve was enhanced when sodium tetraphenylborate (STPB) was used as the titrant; a similar observation has been reported (16).

As a final note, the present titration method can be adapted to measure the equivalent weights of quaternary ammonium compounds and to determine the total charge on the surface of the hair fiber. The apparent equivalent weight of the cationic compounds calculated from the calibration curves is shown in Table II. However, further studies in such areas as pH effects, stability, molecular weight, and determination of the degree of quaternization of the ammonium compounds are needed to evaluate such concepts.

ACKNOWLEDGMENTS

The support of Paula and John Meehan of Redken Laboratories, Inc., is appreciated. The technical assistance of A. Edward Newsom, John N. Bruzas, Ivy L. P. Mai, and Diana C. Toro is acknowledged.

REFERENCES

- (1) C. R. Robbins, *Chemical and Physical Behavior of Human Hair* (Springer-Verlag, New York, 1988), pp. 196–224.
- (2) R. J. Bouthilet and A. Karler, Cosmetic effect of substantive proteins, *Proc. Sci. Sect. Toilet Goods Assoc.*, **44**, 27–31 (1965).
- (3) R. J. Crawford and C. R. Robbins, A replacement for Rubine dye for detecting cationics on keratin, *J. Soc. Cosmet. Chem.*, **31**, 273–278 (1980).
- (4) Y. K. Kamath, C. J. Dansizer, and H.-D. Weigmann, Surface wettability of human hair. I. Effect of deposition of polymers and surfactants, *J. Appl. Polym. Sci.*, **29**, 1011–1026 (1984).
- (5) H.-D. Weigmann, Y. K. Kamath, S. B. Ruetsch, P. Busch, and H. Tesmann, Characterization of surface deposits on human hair fibers, *J. Soc. Cosmet. Chem.*, **41**, 379–390 (1990).
- (6) E. D. Goddard and W. C. Harris, An ESCA study of the substantivity of conditioning polymers on hair substrates, *J. Soc. Cosmet. Chem.*, **38**, 233–246 (1987).
- (7) H. J. White, Jr., and D. L. Underwood, The use of radiotracers to study absorption by hair, *J. Soc. Cosmet. Chem.*, **7**, 198–204 (1956).
- (8) J. A. Faucher and E. D. Goddard, Influence of surfactants on the sorption of a cationic polymer by keratinous substrates, *J. Colloid. Interf. Sci.*, **55**, 313–319 (1976).
- (9) E. D. Goddard, J. A. Faucher, R. J. Scott, and M. E. Turney, Sorption of polymer JR on keratinous surfaces—Part II, *J. Soc. Cosmet. Chem.*, **26**, 539–550 (1975).
- (10) G. V. Scott, Spectrophotometric determination of cationic surfactants with Orange II, *Anal. Chem.*, **40**, 768–773 (1968).
- (11) G. V. Scott, C. R. Robbins, and J. D. Barnhurst, Sorption of quaternary ammonium surfactants by human hair, *J. Soc. Cosmet. Chem.*, **20**, 135–152 (1969).
- (12) L. K. Wang and W. W. Shuster, Polyelectrolyte determination at low concentration, *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 312–314 (1975).
- (13) J. M. Hutter, M. T. Clarke, E. K. Just, J. L. Lichtin, and A. Sakr, Colloid titration: A method to quantify the adsorption of cationic polymer by bleached hair, *J. Soc. Cosmet. Chem.*, **42**, 87–96 (1991).
- (14) B. J. Birch and D. E. Clarke, Surfactant-selective electrodes, *Anal. Chim. Acta*, **67**, 387–393 (1973).

- (15) K. M. Kale, E. L. Cussler, and D. F. Evans, Characterization of micellar solutions using surfactant ion electrodes, *J. Phys. Chem.*, **84**, 593–598 (1980).
- (16) H. H. Y. Oei, I. Mai, and D. C. Toro, Quantitative analysis of anionic or cationic surfactants using a surfactant electrode, *J. Soc. Cosmet. Chem.*, **42**, 309–316 (1991).
- (17) J. Chao, A. E. Newsom, I. M. Wainwright, and R. A. Mathews, Comparison of the effects of some reactive chemicals on the proteins of whole hair, cuticle and cortex, *J. Soc. Cosmet. Chem.*, **30**, 401–413 (1979).
- (18) S. A. Karjala, R. J. Bouthilet, and J. E. Williamson, Some factors affecting the substantivity of proteins to hair, *Proc. Sci. Sect. Toilet Goods Assoc.*, **45**, 6–7 (1966).
- (19) H. Zahn, Chemical processes of the bleaching of wool and human hair with hydrogen peroxide and peroxy acids, *J. Soc. Cosmet. Chem.*, **17**, 678–701 (1966).