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Acid-base characteristics of human hair: Absorption of HCl and NaOH, and the effects on physical properties

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Synopsis

An investigation of the ABSORPTION of HCl and NaOH by HUMAN HAIR is reported. Normal hair absorbs little HCl and NaOH in the range between pH 4 and 10. BLEACHING with H_2O_2 for an hour reduces this range by about 2 pH units from the base side, and the enhanced NaOH absorption is accompanied by a slightly decreased HCl absorption at low pH. Also, bleached hair exhibits significantly faster absorption of both HCl and NaOH. The effects of HCl and NaOH absorptions on the physical properties of hair are investigated via measurements of fiber density, viscoelasticity, interfiber friction and triboelectric behavior and examination of visual and microscopic appearance. The results are mutually consistent and correspond well with the HCl and NaOH absorption characteristics to indicate that normal hair is immune to the actions of HCl and NaOH over a pH range between 4 and 8.

INTRODUCTION

Commercial shampoos span a broad pH range (between 3.3 and 8.0) but there seems to be some subscription to the thought that low pH shampoos are better for hair than those with neutral or alkaline pH. It is often claimed that acid pH brings forth astringent or constrictive effects and consequently enhances structural integrity, luster and manageability of hair. Such claims are based on qualitative and largely subjective information and have perhaps stemmed from the concept of acid-rinses practiced in the days of the soap shampoos. The proponents of low pH shampoos could also have drawn some support from the published values of the isoelectric and isoionic points of human hair. For normal hair, the former is determined to be pH 3.67 by microelectrophoresis (1) and pH 2.45–3.3 by streaming potential measurement (2,3), while the latter is stated to be in the vicinity of pH 6 (4). The actual relevance of such data in reference to the claims of beneficial effects of acid shampoos, however, remains uncertain.

The present investigation entails measurements of the ability of human hair to absorb HCl and NaOH and of the effects of such absorptions on physical properties including fiber density, viscoelasticity, interfiber friction, triboelectric behavior and physical and microscopic appearance.

EXPERIMENTAL

1. ABSORPTION OF HCl AND NaOH

The HCl and NaOH absorption experiments were conducted with three types of human hair:

a. De Meo natural brown;

b. De Meo natural white (blond); and

c. De Meo natural brown, bleached for 1 hour in a 3% aqueous solution of H_2O_2 at pH 10 and 35°C. As a result of this bleaching, cysteic acid increased from 43 to 183 μ moles and ½ cystine decreased from 1400 to 1198 μ moles per gram of hair.

The three types of hair were thoroughly Soxhlet extracted first with a 50/50 chloroform/methanol mixture and then with distilled, deionized water to bring them to an initial state near the neutral pH. The samples were dried, formed into several 1.5 gram specimens and conditioned in a 65% RH, 70°F atmosphere.

The HCl and NaOH absorptions by the specimens at various pH levels in the pH 2–11 range were measured using an automatic titrimeter.

In the procedure, the hair specimen was introduced into HCl or NaOH solution, using 1g:100 ml liquor ratio, at the specified pH level; the volume of 0.01N acid or 0.01N base added from the titrimeter burette to the treatment solution to maintain the pH constant at that specified level was automatically recorded as a function of time. At the pH 2 level, 0.05N acid was used instead of 0.01N in the titrimeter burette because the latter has nominally the same pH as the treatment solution to render titration impossible. The treatment was continued for 24 hours, which was longer than the time required to reach equilibrium in every instance. The specimens were then removed from the treatment baths and dried.

These specimens were highly entangled and were unsuitable for evaluation of physical properties. Therefore, a different set of 8-inch, 1.5 g.wt. tresses of De Meo natural brown hair, precleaned by Soxhlet extraction with a 50/50 chloroform/methanol mixture, were individually immersed for 2–3 hours in aqueous solutions of HCl and NaOH at room temperature, one each at every integral level of pH between 2 and 11. Each tress was subjected to ten such immersions followed each time by drying in an oven at 55°C. The tresses were finally equilibrated overnight in solutions at their respective pH levels. The pH of the solutions used in the final cycle of treatment did not change and therefore equilibration of each tress at its respective pH level was ensured. The tresses were removed from the treatment baths and dried.

2. EVALUATION

Many of the physical tests were conducted only with the brown hair samples treated at pH 2, 4, 7, 9 and 11.

2.1. *Fiber Density*

Fiber density was measured using a density gradient column prepared with toluene (ρ = 0.87 g/cm^3) and carbon tetrachloride (ρ = 1.60 g/cm^3).

Only the hair specimens with no microscopically observable medulla were used for density measurements. The specimens were preconditioned at 22°C, 65% RH before introducing into the gradient column. Several hours were allowed for the specimens to reach floatation equilibrium, and their densities were calculated from the calibration curves via polynomial regression.

2.2. *Viscoelasticity*

Viscoelastic properties were measured using a Rheovibron Direct Reading Dynamic Viscoelastometer. The elastic and loss moduli of the fibers were calculated as

$$E' = [(\Delta F_0/d)/(\Delta L_0/L_i)]\sqrt{1+\tan^2\delta}, \quad \text{and}$$

$$E'' = [(\Delta F_0/d)/(\Delta L_0/L_i)]\tan\delta/\sqrt{1+\tan^2\delta},$$

where ΔF_0 is the amplitude of the dynamic force output, d is the linear density of the specimen, ΔL_0 is the amplitude of the dynamic displacement input, L_i is the specimen length, δ is the phase angle by which the output lags behind the displacement. The measurements were made with $\Delta L_0 = 1.580 \times 10^{-3}$ cm, dynamic frequency = 110 Hz, and at 22°C and 65% RH.

2.3. *Interfiber Friction*

Interfiber friction was measured by the well-known fiber-twist method (5). In the procedure, a pair of fibers were twisted together $n(=2)$ times at a small constant angle β, a tension T_1(=6.06 gram-force) was applied to each fiber and the force T_2 required to set and maintain the fiber in motion relative to one another was measured. Measurements were made in both against-scale (tip-tip) and with-scale (root-root) directions and at two levels of humidity (65% RH and wet).

2.4. *Triboelectric Behavior*

Triboelectric behavior was measured using a Faraday pail and cage connected to an electro(coulomb) meter.

In the procedure, the hand-held tress sample was stripped of any unbalanced charge using a deionizing bar, brushed or combed 20 strokes with a similarly deionized brush or comb and dropped into the Faraday pail. The magnitude and the polarity of the resultant charge was recorded. A nylon brush, an aluminum comb and a plastic (nylon) comb were used in these experiments. Measurements were made at the following intervals and conditions:

a. Immediately following the final cycle of treatment, tresses dried under N_2 flow: O-HR-Dry-N_2.

b. Immediately thereafter, tresses dried in an oven at 55°C: O-HR-Dry.

c. After conditioning in a standard atmosphere (22°C, 65% RH) for 24 hours: 24 HR-65% HR.

d. Two days later, tresses dried in the oven at 55°C: 72 HR-Dry.

2.5. Visual Appearance

The tresses were arranged in a random order against a white background. Each member of a panel of 7 women and 9 men was asked to assign each tress a rank between 1 (the worst) and 10 (the best) depending on its color and luster.

2.6. Microscopic Appearance

Fiber specimens from the brown, the blond, and the bleached hair tresses were examined under a scanning electron microscope for definition of the cuticle structure. Wet-mounted fiber specimens were observed under an optical microscope for cuticle lifting.

RESULTS AND DISCUSSION

1. ABSORPTION OF HCl AND NaOH

From the HCl and NaOH absorption curves (i.e., volume vs. time) for the brown, the blond, and the bleached hair, the following quantities were calculated:

a. quantity of HCl and NaOH absorbed at equilibrium, m_∞(m moles/g of hair)

b. initial absolute and relative velocity constants, K and K', as defined by

$$\left.\begin{aligned} m(t) &= K\sqrt{t} \\ m(t)/m_\infty &= K'\sqrt{t} \end{aligned}\right\} t \leq 20 \text{ min.}$$

The absolute velocity constants (K) are shown in Figure 1. The bleached hair exhibits higher K compared with the normal hair. The lower disulfide cross-link density in the bleached fiber, as evidenced in data from amino-acid analysis of the bleached hair as well as in some published literature (6), perhaps permits rapid swelling to enhance the absorption processes.

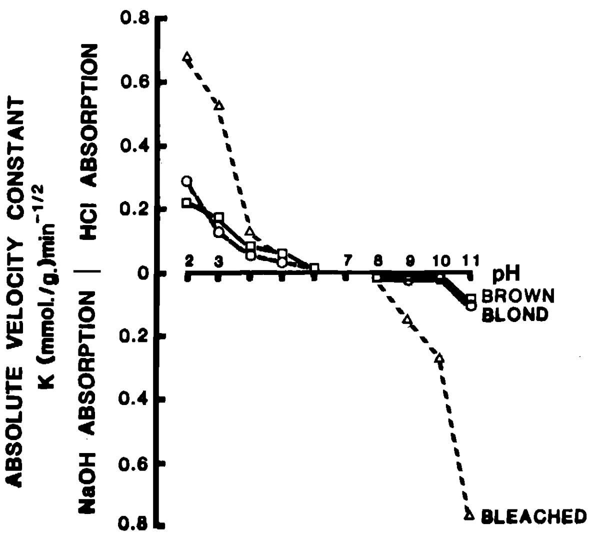

Figure 1. Absolute velocity constants for initial stages of HCl and NaOH absorptions.

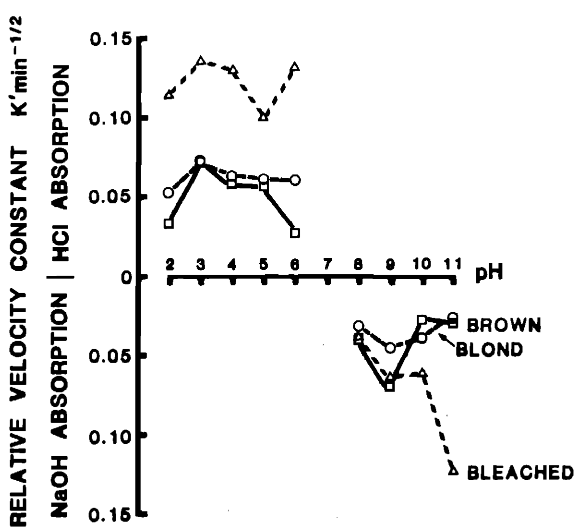

Figure 2. Relative velocity constants for initial stages of HCl and NaOH absorptions.

The relative velocity constants (K') are shown in Figure 2. The following inferences may be made from these results. First, the K' for HCl absorption show no definite dependence on pH, suggesting that the diffusion coefficient for the process may be independent of concentration. Second, K' for the HCl absorption by the bleached hair appear to be substantially higher than the corresponding values for the normal hair. Since bleaching is known to increase hydrophilicity of the fiber surface (7) and also increase the diffusion constant (8) and swelling (9, p. 183), the above results are perhaps attributable to faster saturation of the surface with protons followed by their faster diffusion into the bleached hair compared with the normal hair. We have made a similar observation in reference to methylene blue dye absorption by normal and bleached hair. In the pertinent experiments, spectrophotometric measurement of methylene blue dye depletion from a finite 1×10^{-5} M dye-bath buffered to 7 pH, showed that at a liquor ratio of 1g:667 ml the initial relative velocity constant is 0.208 $min^{-1/2}$ for 1-hour peroxide-bleached hair which is substantially greater than the value of 0.158 $min^{-1/2}$ for the normal hair; optical microscopic examination of the cross-sections of the fibers dyed to equilibrium gave indication of significant radial diffusion of the dye into the bleached fibers in contrast with the peripheral- or ring-dyeing of the normal fibers. Finally, the relative velocity constants for the base absorption by the bleached hair do not seem to differ much from those for the normal hair except at 11 pH. This is perhaps a reflection of the susceptibility of the bleached hair fibers to rapid tertiary-structural disintegration under such alkaline conditions.

The equilibrium absorptions of HCl and NaOH, shown in Figure 3, resemble those of wool (10, p. 188, 11, p. 354). The characteristic sigmoidal shape of the absorption curve shows the existence of a broad pH range where little or no absorption takes place. For the normal hair, the range is between pH 4 and 10. The HCl absorption behavior is very similar to that reported by Breuer and Prichard (12) for normal hair. The bleached hair appears to absorb slightly less HCl; this effect of bleaching is qualitatively consistent with the available information on the acid-binding capacity (13), but its magnitude appears to be insignificant under the conditions involved here (i.e., pH $\geq$ 2). The

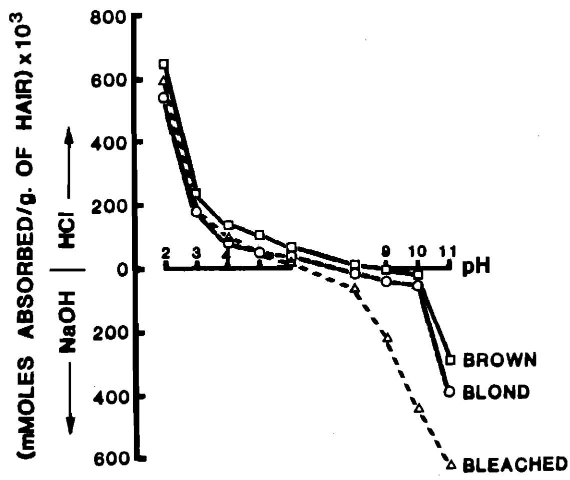

Figure 3. Equilibrium HCl and NaOH absorptions by human hair.

NaOH absorption characteristics of the bleached hair, however, differs significantly from that of the normal brown hair. It registers absorptions of a notable quantity of NaOH at a pH as low as 9 and increasing quantities thereafter. As with HCl absorption, the observed effect of bleaching on NaOH absorption is consistent with the published literature (13).

2. EFFECTS ON PHYSICAL PROPERTIES

2.1 Fiber Density

The effects of HCl and NaOH treatments on the brown hair fiber density are shown in Figure 4. The results appear to be coherent with the HCl and NaOH absorption behavior (Figure 3). Between pH 4 and 9, hair absorbs very little HCl and NaOH and causes no change in its structure and hence its density. At pH 2 and 11, large quantities

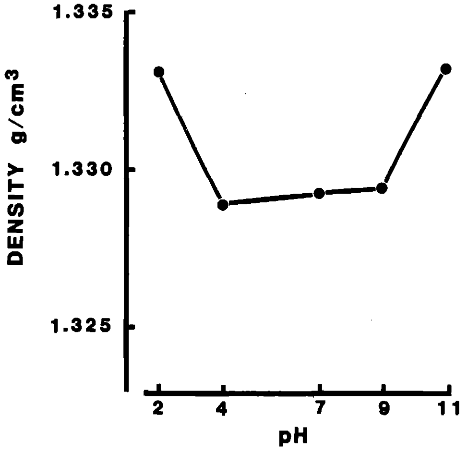

Figure 4. Effect of pH on hair fiber density.

of HCl and NaOH are absorbed to cause structural changes and the density increases from the normal value of about 1.329 g/cm^3 to about 1.333 g/cm^3. Analysis of variance and multiple range tests of the density data have shown this change to be highly significant.

The nature of this structural change is not known with certainty, but acid and alkaline hydrolysis may be assumed to be the mechanism. It is noteworthy that hydrolysis of wool fibers with proteolytic enzymes such as trypsin, papain, pepsin and ficin is shown to cause the density to increase from the normal value of 1.306 g/cm^3 to 1.32-1.33 g/cm^3 (14). Such treatments are far more severe than the HCl and NaOH treatments of the present investigation.

2.2 Viscoelasticity

The effects of HCl and NaOH treatments on elastic and loss moduli of the hair fibers are shown in Figure 5. Like the density data, these results cohere well with the HCl and

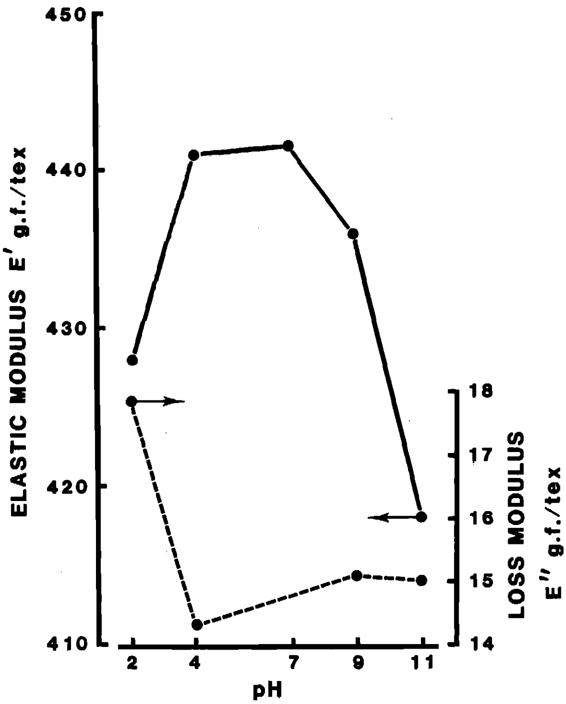

Figure 5. Effect of pH on viscoelastic properties.

NaOH absorption behavior (Figure 3). The hair fiber remains unaffected by treatments between pH 4 and 9, but at pH 2 and 11 significant structural changes seem to take place, giving rise to higher deformational compliance. The substantial decrease in E' is accompanied by an increase in E'' at pH 2 but not at pH 11, suggesting that the molecular mechanisms induced by the acid treatment are different from those by the alkali. Analysis of variance and multiple range tests of the E' and E'' data have shown the aforementioned effects to be statistically significant.

These results may be considered to be consistent with the numerous observations made by others on deformational response of wool (15, pp. 56, 57, 131) and on swelling of hair (9, pp. 164, 182).

2.3 Interfiber Friction

The effects of HCl and NaOH treatments on interfiber frictional force (T_2) are shown in Figure 6. The against-scale (tip-tip) friction is higher than the with-scale (root-root)

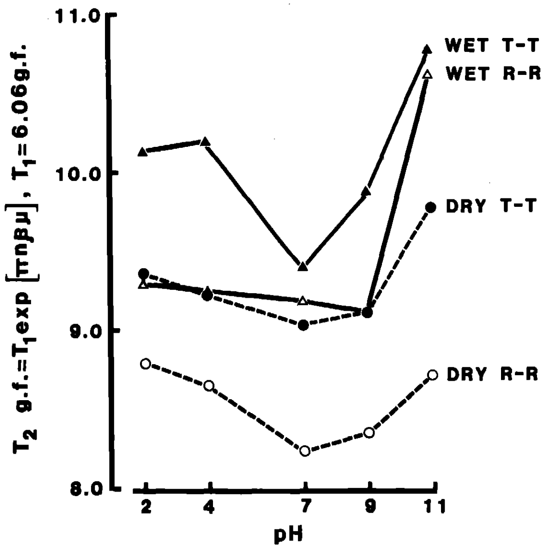

Figure 6. Effect of pH on inter-fiber friction.

friction and wet friction is higher than the dry friction, as expected; the former represents the directional frictional effect and the latter arises from lateral swelling of the wet fiber. Similar observations are recorded in the literature in reference to wool (10, p. 28) and hair (9, pp. 185–187).

There is some evidence of increase in friction by treatment at pH 11 and a minimum in the vicinity of pH 7. The alleged astringent effects of acid pH on hair finds little support in the data.

2.4 Triboelectric Behavior

The effects of HCl and NaOH treatments on triboelectric behavior are shown in Figures 7(a)–7(d). Several inferences may be drawn from these results:

a. The polarity and magnitude of triboelectric charge on hair show definite dependence on pH. The acid-treated hair acquires excessive negative charge in every instance. There exists a tendency for the charge to gradually change from a large negative value to a large positive value with increasing pH. The polarity switches from negative to positive in the vicinity of pH 8.

b. The method of drying seems to have no influence on the charge-pH relationship.

c. Preconditioning the tresses at 65% RH reduces the magnitude of the charge as

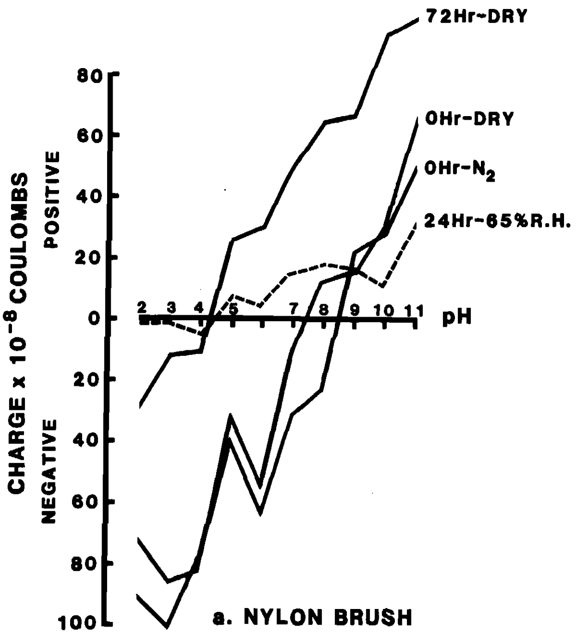

Figure 7(a). Effect of pH on triboelectric properties, using a nylon brush.

expected. The gradual shift of polarity from negative to positive with increasing pH persists, and in the case of semiconductor grooming objects (nylon brush and plastic comb) the charge vs. pH curve shifts by 3 or 4 pH units towards the acid side. Upon subsequent drying, this shift of the curve is maintained and the magnitude of the charge is increased as expected.

d. The unusually low charge for the tress treated at pH 2 is inconsistent with the fairly well-defined trend in charge-pH relationship. It is perhaps attributable to surface changes associated with absorption of a large quantity of HCl.

e. The foregoing observations are unprecedented. Lunn and Evans (16) assert that the

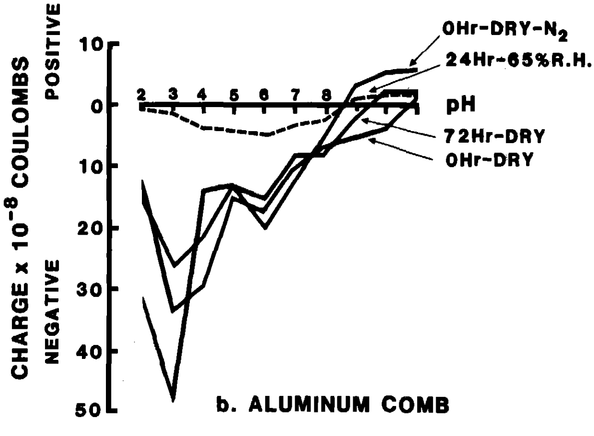

Figure 7(b). Effect of pH on triboelectric properties, using an aluminum comb.

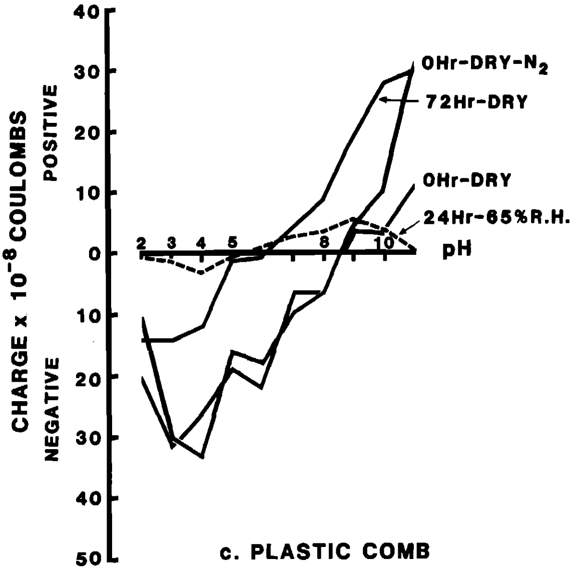

Figure 7(c). Effect of pH on triboelectric properties, using a plastic comb.

charge generated on hair by combing is of positive polarity and identify their observation to be consistent with triboelectric series and theory of asymmetric rubbing (17). Other authors (18–20), in reference to triboelectric properties of wool and other polar polymers, have made conflicting statements, but in essence their results are in direct contrast with our observations. According to them, the acid-treated keratin becomes postively charged and the opposite happens with base

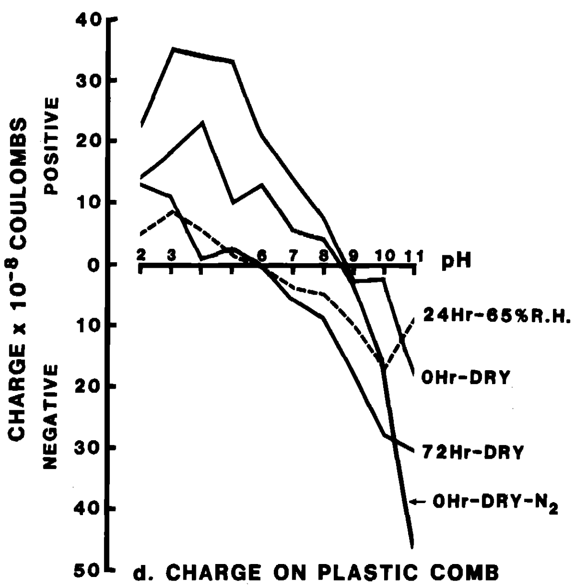

Figure 7(d). Effect of pH on triboelectric properties, using a charged plastic comb.

treatment. They assume that triboelectrification results from ionic conduction, and state that the conduction of mobile ions in the fibers (20) conforms to the boundary potential theory (18–20). Our results cannot be explained without additional experiments aimed towards determination of charge transport mechanisms in hair fibers.

2.5 *Visual Appearance*

The results of evaluation of physical appearance (color and luster) of the acid-base treated tresses are shown in Table I. The table contains the average rank for each tress

Table I
Effect of Acid-Base Treatment of Visual Appearance of Brown Hair Tresses, and Analysis of the Data[1]

Treatment pH	Average Rank of Appearance (1 = Worst, 10 = Best)
2	6.5
3	6.1
4	6.4
5	7.1
6	6.9
7	6.4
8	6.7
9	2.7
10	3.2
11	3.1

[1] H_0: $\tau_1 = \ldots\ldots = \tau_{10}$ where τ is the pH effect, $n = 16$, $k = 10$

$$S' = 12 \sum_{j=1}^{k} \frac{(R_j - nR..)^2}{[nk(k+1)] - [1/(k-1)]\left[\left(\sum_{j=1}^{g_i} t^3_{ij}\right) - k\right]} = 81.08$$

$Pr\,[S' \geq \chi^2 (k-1, \alpha)] \leq 0.01$

and the essential statistics from a distribution-free rank sum test due to Friedman, Kendall and Babington Smith (21). The pH of the treatment is seen to have significantly influenced the appearance of the hair. Only the three tresses treated at pH $\geq$ 9 suffered identifiable change in appearance; qualitatively, these tresses appeared considerably lighter in color than the others, but the luster differences could not be identified.

2.6 *Microscopic Appearance*

Examination of the hair fibers under SEM gave no evidence of adverse effects of HCl and NaOH except very slightly at pH 11. The bleached fibers showed notable surface degradation at pH $\geq$ 9.

Similar observations were made with the wet-mounted fibers under optical microscope. All the brown and the blond hair showed normal cuticles, but the bleached hair treated at pH $\geq$ 9 showed ill-defined surface. The lifting of the cuticles did not appear abnormal in any of the fibers.

CONCLUSIONS

Bleached hair exhibits significantly higher absolute rates of absorption of HCl and NaOH compared with normal hair. The relative rates or diffusion coefficients of bleached hair are significantly higher than those of normal hair for absorption of HCl under all conditions and for absorption of NaOH at 11 pH. The HCl and NaOH absorption behavior of hair is very similar to that of wool. There exists a broad pH range in which hair absorbs little or no HCl and NaOH. For normal hair the range is pH 4–10. Bleaching narrows the range by about 2 pH units from the base side.

The density of normal hair fiber remains unaffected by treatment with HCl or NaOH in the pH 4–9 range. Under the extreme conditions of pH 2 and 11, the density increases significantly.

Viscoelastic properties also show a similar tendency. They change little in the pH 4–9 range. At pH 2, the elastic modulus decreases and the loss modulus increases. At pH 11, the elastic modulus decreases with no change in the loss modulus.

There is some evidence of a slight increase in interfiber friction at pH 11 and of a probable minimum near neutral pH.

Triboelectric behavior of hair shows pronounced dependency on pH. The low pH treated hair is susceptible to acquiring negative charge. The charge changes from a large negative value to a large positive value with increasing pH. Under dry conditions, the polarity of the charge shifts from negative to positive in the vicinity of pH 8.

Visual appearance of hair remains unaffected from pH 2–8. Hair treated at pH $\geq$ 9 suffers noticeable discoloration.

Scanning electron and optical microscopic appearance show that normal hair is not affected by pH and that bleached hair undergoes surface degradation at pH $\geq$ 9. No conclusive evidence of a constrictive effect by acid pH or a distending effect by neutral or alkaline pH could be found.

These physical properties are mutually coherent and correspond well with the HCl and NaOH absorption characteristic of hair to suggest that normal hair remains immune to the actions of HCl and NaOH over a broad range of pH, approximately between 4 and 8.

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