J. Soc. Cosmet. Chem., **28**, 695–704 (November 1977)

The tensile properties of hair fibers in 1-propanol water mixtures

D. LU* and M. M. BREUER† *Personal Care Division, The Gillette Company, Gillette Park Boston, MA 02106.*

Received January 3, 1977.

Synopsis

The stress–strain curves of intact hair fibers immersed in aqueous 1-propanol solutions were measured as functions of 1-propanol concentration, pH and temperature. Plots of the tensile forces at given extensions against the propanol concentrations show minima at about 50 per cent propanol; these become more pronounced at low pH values and at higher temperatures.

The experimental results can be interpreted by assuming that two additive molecular processes are responsible for the elasticity of hair: conformational changes of the polypeptide chains and electrostatic interactions between the various ionic side chains. The presence of 1-propanol in low concentrations accentuates the importance of the latter process by diminishing the value of the effective dielectric constant inside the hair structure. At high propanol concentrations, however, the dehydration of the fibers increases the relative contribution of the conformational changes and brings about a strengthening of the hair.

I. INTRODUCTION

Alcohols are extensively used in the formulation of hair care products. Although many of the technologically important properties of keratin fibers have been known to be affected by exposure to alcohols (1, 2) (e.g., the elastic modulus and the temperature of supercontraction both change when hair is immersed in aqueous alcoholic solutions (3)), the mechanisms responsible for these processes are still unclear. Essentially, two hypotheses have been formulated to account for these phenomena. Blankenberg and Zahn (2) suggested that the alcohols break hydrophobic bonds and thus, weaken the keratin structure. Breuer (4), on the other hand, postulated that the presence of alcohols in the keratin fiber alters the transition equilibrium between the organized and amorphous regions of keratin and, therefore, affects the stress–strain characteristics of the fibers.

Neither of these hypotheses allowed for the possibility that the absorption of alcohols by hair might also affect the electrostatic interactions within the fibers and, thus, could affect their mechanical properties.

*6133 Hughes Aircraft Co., 11940 West Jefferson Blvd., Culver City, CA 90230.
†Gillette Research Institute, 1413 Research Blvd., Rockville Md. 20850.

Recently, we have obtained experimental data suggesting that, indeed, this might be the case. The present communication reports these findings.

II. EXPERIMENTAL

A. MATERIALS

Intact hair was obtained from the DeMeo Company.* Before use, it was shampooed once with an anionic shampoo-pH 4.3,† rinsed and dried in air. Reagent grade 1-propanol was used for preparing the solutions. The buffers used were pH 7.0, pH 7.4 phosphate buffers (0.05 *M*), and pH 2 HCl solution, respectively.

B. METHODS

One-in. long hair fibers were mounted onto plastic tabs using an epoxy glue‡ and soaked overnight in pH 7.0 buffer. First, a reference stress–strain curve was obtained for each fiber; i.e., the fiber was stretched to 20 per cent extension (at 1 in./min) while immersed in pH 7 buffer at 20°C (Reference curve No. 1). A table model Instron Extensometer was used with standard procedures being employed.

Subsequently, the fiber was relaxed in pH 7.4 buffer for 24 h, equilibrated in the appropriate proponal-water mixture and the stress–strain isotherm measured while the fiber was immersed in the solution at the appropriate temperature. A 24-h period was allowed for equilibration of each fiber in the appropriate water-alcohol mixture, since previous work has ascertained that this time period was sufficient to reach equilibrium (5). After completion of the measurements, the fibers were again relaxed in pH 7 buffer at 20°C for 24 h and a second reference stress–strain curve obtained using identical experimental conditions to those employed during the determination of the first calibration curve (reference curve No. 2).

III. RESULTS

Although ethanol is the most widely used alcohol in cosmetic and toiletry products, we chose 1-propanol for our investigations. Our choice was motivated by the finding of previous investigators who showed that immersion into 1-propanol/water mixtures have the largest effects, among the alcohols, on the properties of keratin fibers (1–4).

In order to eliminate, as far as possible, errors which were due to fiber to fiber variations, the forces were normalized, i.e., divided by the force obtained on the same fiber at the corresponding extension during the first reference cycle. The symbol f′ denotes the normalized force (i.e., the ratio f/fo) where f and fo are the two forces measured on the same fiber at a given strain level under the given experimental conditions and dur-

*DeMeo Brothers, New York®.

†Earth Born Green Apple Shampoo®, Personal Care Division, the Gillette Co., Boston, MA.

‡Twoton glue®, Descon Corp., Danvers, Mass.

Table I
Ratios of the Tensile Forces of Hair Fibers in pH 7 Buffer Solutions Before and After the Experiments

Treatment Exposure to W/W per cent Propanol	f_0'/f_0*				T°C
	pH 2.0		pH 7.4		
0	0.89	0.92	—	1.05	60
30	0.86	0.89	1.02	0.92	60
50	0.94	0.99	0.87	0.95	60
80	0.89	—	0.97	0.93	60
0	0.94	0.98	1.03	1.02	40
30	1.00	1.04	1.00	1.00	40
50	1.03	1.05	0.98	1.00	40
80	1.00	1.00	1.00	1.00	40
0	0.98	0.90	0.95	0.93	20
30	0.93	0.97	0.93	0.93	20
50	0.93	0.95	0.89	0.94	20
80	0.95	0.96	0.92	0.93	20

*f_0 and f_0' denote the values of the elastic forces in the first and second reference cycles, respectively.

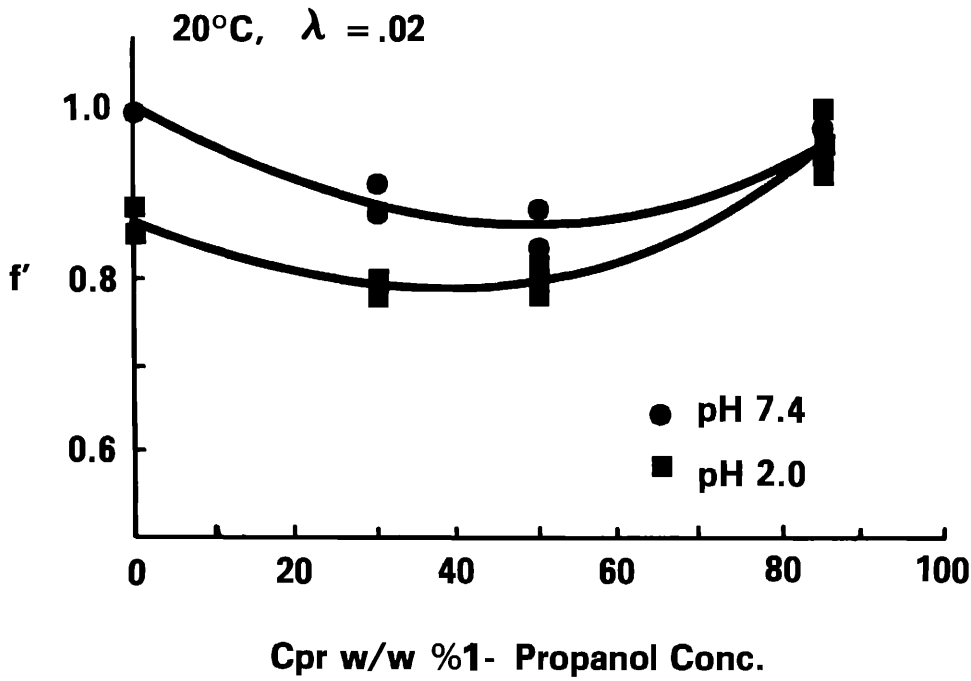

Figure 1. Plot of normalized force f′ of intact hair fibers against 1-propanol content of immersion liquid at 20°C and extension λ = 0.02

ing the first reference cycle, respectively. The values of the normalized forces were reproducible within an error of ±4 per cent.

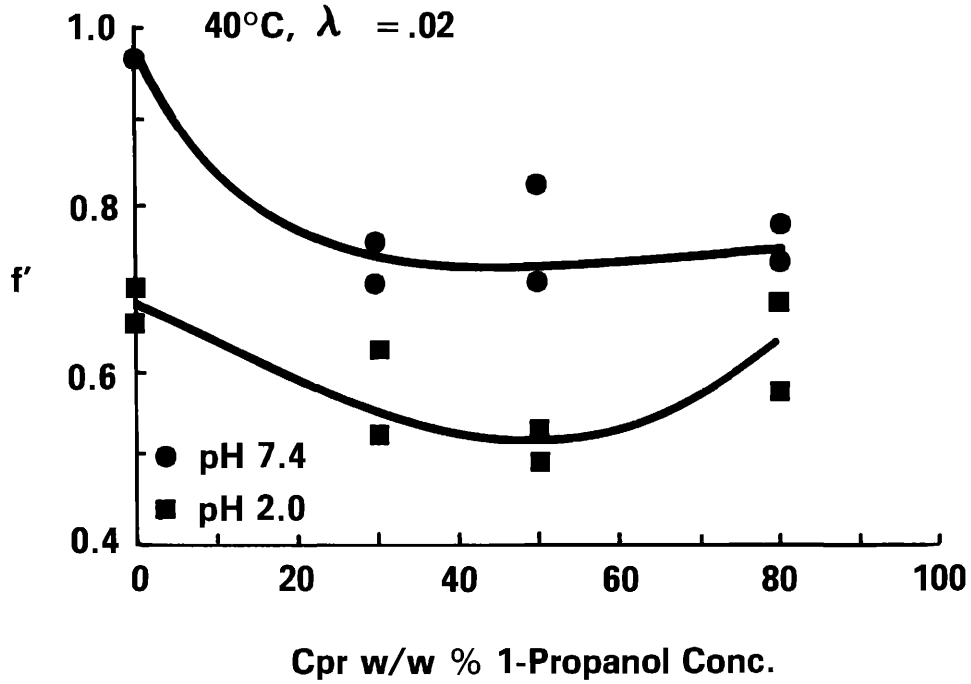

Figure 2. Plot of normalized force f′ of intact hair fibers against 1-propanol content of immersion liquid at 40°C and extension λ = 0.02

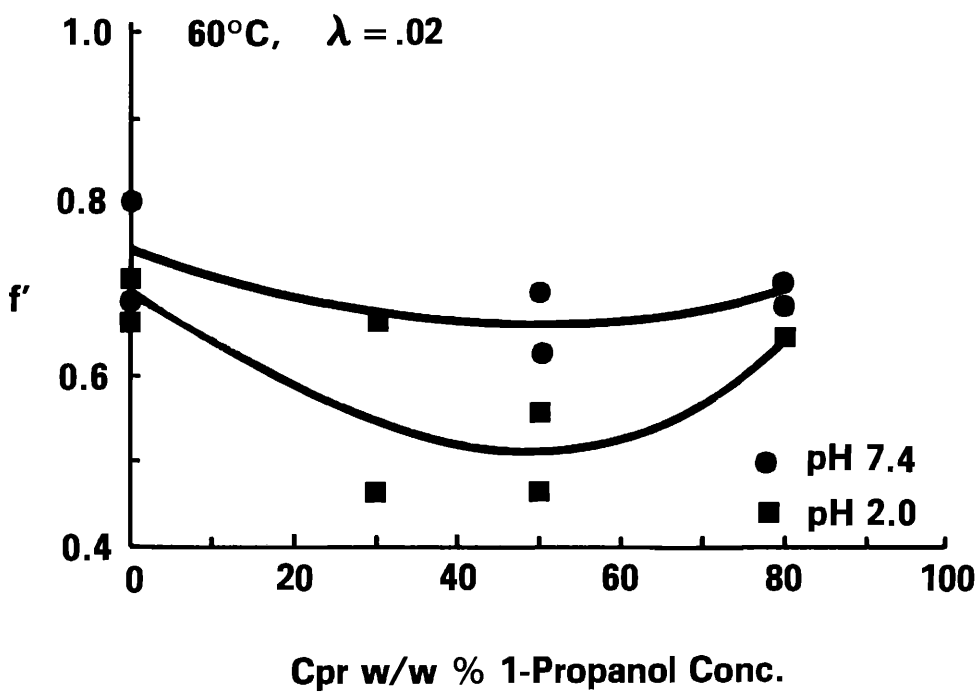

Figure 3. Plot of normalized force f′ of intact hair fibers against 1-propanol content of immersion liquid at 60°C and extension λ = 0.02

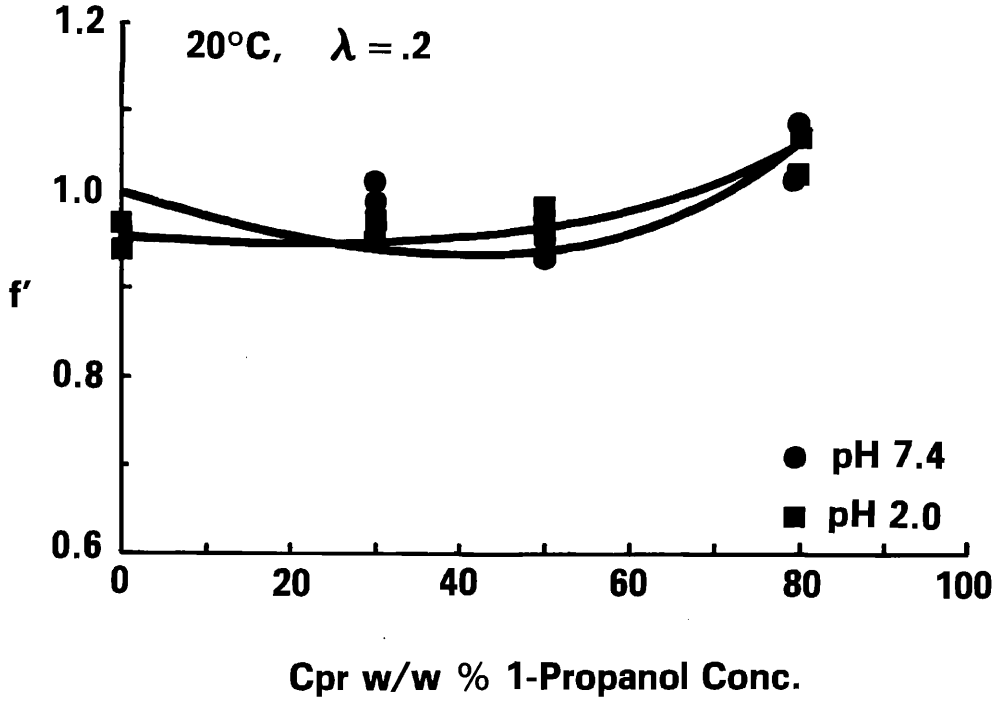

Figure 4. Plot of normalized force f′ of intact hair fibers against 1-propanol content of immersion liquid at 20°C and extension λ = 0.2

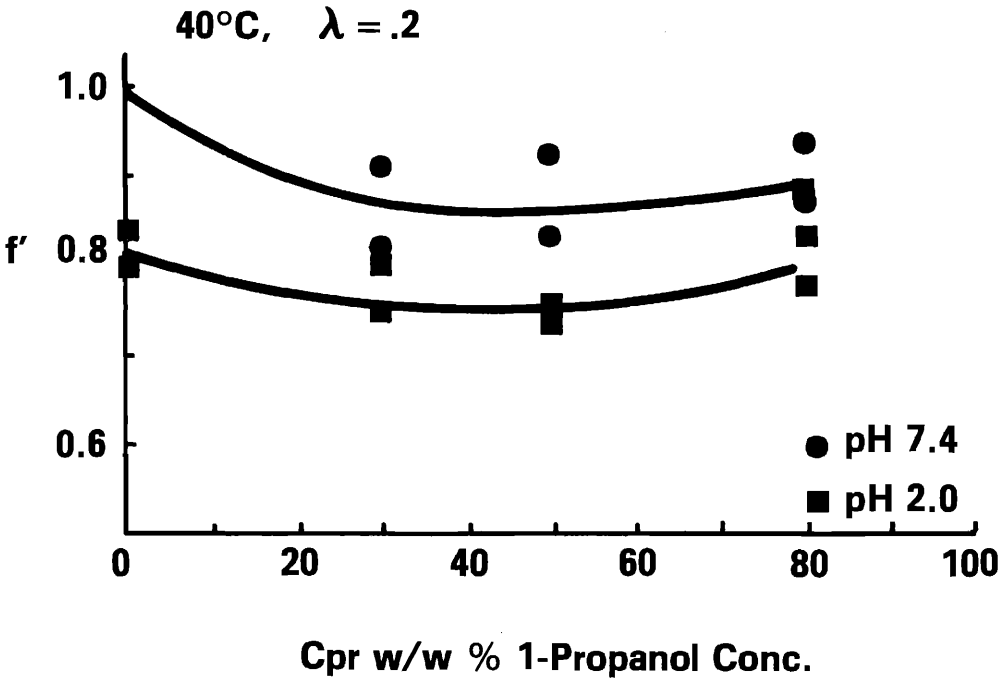

Figure 5. Plot of normalized force f′ of intact hair fibers against 1-propanol content of immersion liquid at 40°C and extension λ = 0.2 (This figure is reproduced with permission of John Wiley & Sons where it originally appeared in the Interpretation of the Mechanical Properties of Wool, *Appl. Polym. Symp.*, **18**, 775–94 (1971), by J. W. S. Hearle, B. M. Chapman and G. S. Sethi).

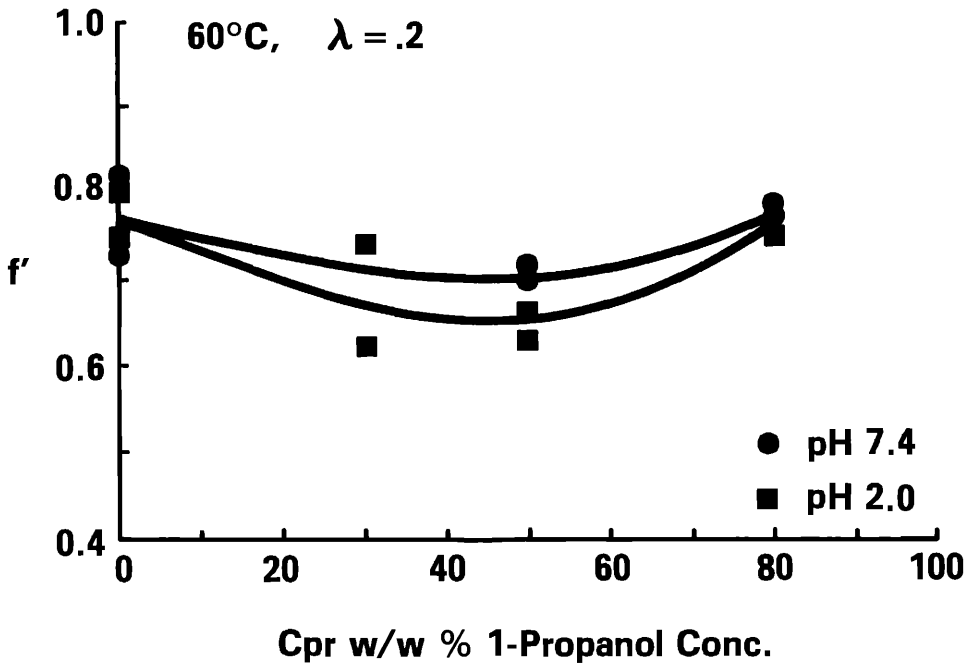

Figure 6. Plot of normalized force f′ of intact hair fibers against 1-propanol content of immersion liquid at 60°C and extension λ = 0.2

None of the treatments caused any irreversible changes in the fibers. We ascertained this fact by comparing the forces measured during the first and the second reference cycle at the same strain level. Allowing for the experimental error of the technique, no differences were found (Table I). In view of the high reproducibility of f′ values, the use of a limited number of fibers for each experimental condition appeared justified to us.

In three series of experiments, we determined the values of f′ as respective functions of temperature, pH and 1-propanol concentration. The results are shown in Figs. 1–6, where the values of f′ are plotted against C_{pr}, the propanol concentration for two pH values (pH 2.0 and pH 7.4) at three temperatures (20, 40, and 60°C).

For a given temperature and pH, increasing the propanol concentration initially reduces the value of f′. As the propanol concentration is further augmented, however, the value of f′ passes through a minimum (at about C_{pr} = 50 per cent) and then again increases.

For a given propanol concentration, the values of f′ are considerably lower at pH 2.0 than at pH 7.4. Raising the temperature from 20° to 40°C enhances the pH effects, i.e., the differences between the values of f′ at pH's 7.4 and 2.0. Finally, all the effects described are more pronounced at low extensions than at higher strain levels.

IV. DISCUSSION

An interpretation of these experimental results can be best considered in the context of a model previously suggested for hair structure (6, 7) (Fig. 7). Accordingly, keratin

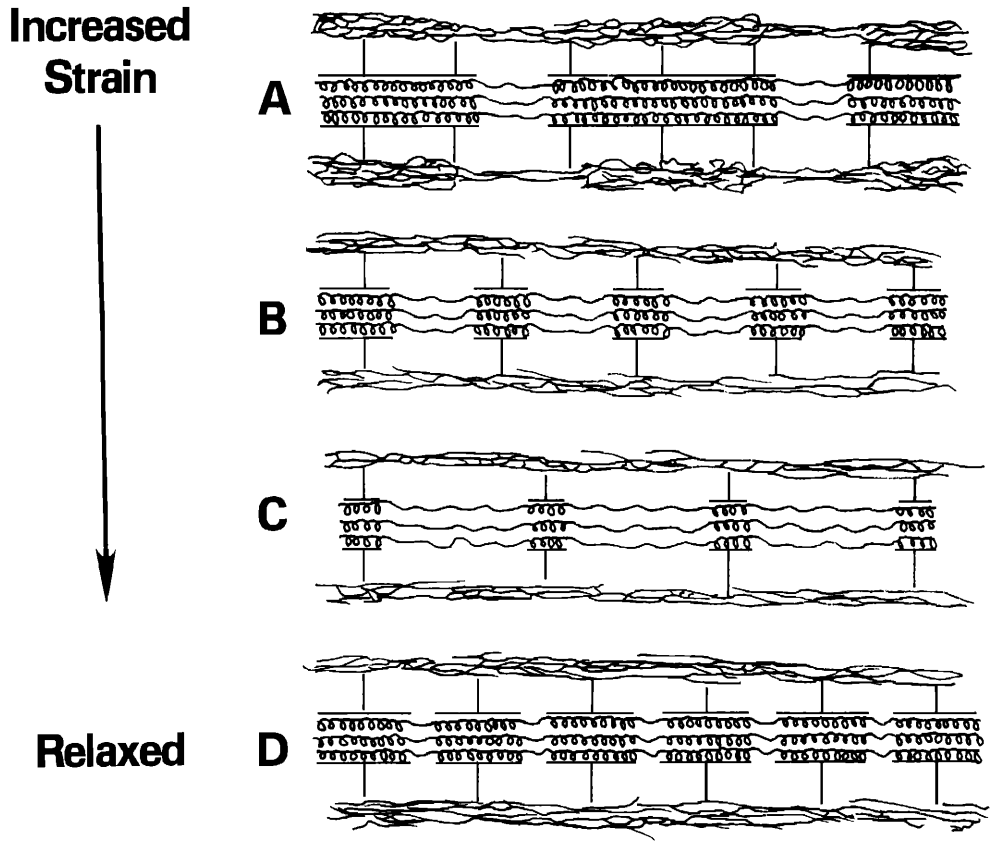

Figure 7. A Keratin structure at various points of stress–strain curve. A → C represent stages of fiber structure at increasing strainings; D shows situation after fiber has been allowed to relax to lower strain level. Spirals, "wiggly" lines, and fuzzy regions denote α-helices, unwound polypeptide chains and matrix, respectively (reproduced with permission from ref. 7)

fibers are regarded as crosslinked polyelectrolyte gels consisting of partially crystalline (α-helical) polypeptide chains, which carry both positively and negatively charged groups attached to the main chains.

Application of an axial stress extends the network, resulting in conformational changes of the polypeptide chains (8), and in increased distances between the various charged groups attached to the polypeptide chains. In most instances, depending on the pH of the surrounding medium, either an excess of positive or negative groups is present in the hair fiber. Consequently, straining of the fiber decreases its electrostatic energy (6).

In accordance with this model, G_t the free energy of an unstrained fiber can be expressed as the sum of two terms: G_{st} the structural and G_{es} the electrostatic free energies (8).

$$G_t = G_{st} + G_{es} \tag{1}$$

Since f_{sr} the structural and f_{es} the electrostatic contributions to the total force, are defined as (9)

$$f_{st} = \frac{1}{1_0}\left(\frac{\partial G_{st}}{\partial \lambda}\right)T, P$$

$$f_{es} = -\frac{1}{1_0}\left(\frac{\partial G_{es}}{\partial \lambda}\right)T, P \quad (2)$$

where f_t the total forces resisting the straining of hair, is

$$f_t = f_{st} + f_{es} \quad (3)$$

and λ denotes the extension ratio

$$\lambda = \frac{1}{1_0} \quad (4)$$

and 1 and 1_0 represent the length of the fiber in the strained and unstrained state, respectively.

Using statistical mechanics, the values of f_{st} and f_{es} can be expressed in terms of molecular quantities. Thus, assuming that the structural contribution of the elastic force is due to a change of the polypeptide chains from α to β conformation, the value of f_{st} is given by (9)

$$f_{st} = \frac{\Delta G_0}{\Delta L_0} \quad \frac{kT}{\Delta L_0} \ln r \quad (5)$$

where ΔG_0, ΔL_0 are the standard free energy and the fiber length change involved when a unit weight of fiber changes from α to β conformation. The function r depends on the extent of change; its value has been previously calculated as a function of extension (10).

The value of f_{es} can be derived from the polyelectrolyte model of hair and can be expressed as (9)

$$f_{es} = n\frac{\gamma^2\epsilon^2\kappa}{D\lambda}\left[\frac{1}{1+\lambda A} - \frac{1}{\lambda A}\ln(1+\lambda A)\right] \quad (6)$$

where n equals the number of molecular chains in unit weight of fiber: γ equals the net charge of an average molecular chain; ϵ equals the electronic charge; D equals the dielectric constant; κ equals the Debye parameter (i.e., the reciprocal of the radius of the ionic atmosphere); λ equals the extension ratio; A equals $1_0\kappa$; and 1_0 equals the average contour length of an unstrained molecular chain in the network.

When hair samples are immersed in aqueous solutions of propanol, limited amounts of propanol (up to about 2 mol/1000 g) are absorbed by the hair fiber (5). At the same time, due to the lowering of water activity, the fibers gradually dehydrate (5). These two processes affect the values of f_{st} and f_{es}, but to different extents. The increase in the propanol content and the simultaneous decrease of water in hair diminishes D, the effective dielectric constant inside the fiber (11) and, thus, increases the value of f_{es}. This process is expected to be more pronounced at pH 2 than at pH 7, since the net charge of the fibers is greater at the lower pH value (for titration curves of keratin, see (12)).

On the other hand, dehydration of the hair fiber shifts the α–β conformational equilibrium towards the α form and thus, increases the force required for straining the fiber (13), i.e., increases the value of f_{st}. The pH of the solution should not affect this latter process.

It is also instructive to consider, in light of this model, some of the X-ray data which have been obtained on keratin fibers containing increasing amounts of propanol. Feughelman and Snaith (14) and later Heideman and Halboth (15) measured the changes occurring in the spacing of the interhelical distances in keratin fibers and found that the spacing of 9.3 Å increases when the propanol concentration is augmented in the immersion liquid. According to these authors, the 9.3 Å spacing corresponds to the distances between the helices in the protofibrils. The increases in this spacing, therefore, suggests that the propanol penetrates the protofibrils and, in doing so, pries the polypeptide helices apart. A similar explanation was suggested by Nemetschek (16) when interpreting the low angle X-ray data of collagen treated with various alcohols.

The findings that neither an increase of alcohol concentration beyond 50 per cent nor the changing of the pH from 6 to 1 affect the 9.3 Å spacing (15) suggest that most of the ionic groups are situated on the surfaces of the protofibrils and in the interior of the protofibrils electrostatic effects do not exert any serious influences.

Raising the temperature from 20 to 60°C affects the absolute values of f′, but does not change the overall shape of the f′ versus C_{pr} curves. This result is in agreement with previous data which indicated that propanol absorption is hardly at all affected by temperature (10).

V. CONCLUSIONS

The force resisting straining of hair is governed essentially by two types of molecular processes: (a) structural changes (α–β transition); and (b) changes in the electrostatic energy of fiber as a consequence of the increase in the interionic distances. These two processes depend differently on environmental factors (i.e., temperature, pH, propanol concentrations).

Our experimental results, presented in this paper, suggest that exposure of hair to aqueous propanol solutions of increasing concentrations first weakens the fibers by increasing the electrostatic repulsion forces between the similarly charged side chains. At higher propanol concentrations ($>$ 50 per cent w/w), however, hair becomes stronger, owing to the dehydration of the fiber which makes the structural conformational changes of the polypeptide chains more difficult.

The experimental results can be explained, at least in qualitative terms, by a molecular model which regards keratin as a partially crystalline crosslinked polyelectrolyte gel.

A quantitative interpretation of the forces in terms of this model necessitates the assignments of arbitrary values to many molecular quantities (e.g., the effective dielectric constant in hair, its dependence on water and propanol uptake, the value of κ inside the hair structure). Since none of the quantities are known to any degree of reliability at this time, this exercise does not seem profitable. Similar conclusions were obtained by Wolfram and Milligan when investigating the tensile properties of esterified and acylated wool (17).

VI. ACKNOWLEDGMENTS

We wish to thank Ms. Irene Cushman for her assistance in the experimental work and Doctors L. Wolfram and F. Girard for helpful suggestions.

REFERENCES

(1) J. C. Atkinson, A. Filson, and J. B. Speakman, *Nature,* **184,** 444–5 (1959).
(2) H. Zahn and G. Blankenburg, Action of alcohol—water mixtures on wool, *Textile Res. J.,* **34,** 176–7 (1964).
(3) G. Blankenburg, Tensile properties and supercontraction of wool keratin in aqueous alcoholic solutions, *Melliand Textilber.,* **48,** 686–90 (1967).
(4) M. M. Breuer, The effect of alcohols on the mechanical properties of keratin and collagen, *Proceedings, First European Biophysics Congress, Vienna,* **5,** 449–54 (1971).
(5) M. M. Breuer and J. C. Bell, The binding of aliphatic alcohols to collagen and keratin, *J. Colloid and Interfacial Sci.,* **37,** 714–20 (1971).
(6) M. M. Breuer, Acid titration of keratin fibers and its implication to the fiber structure, *Trans Faraday Soc.,* **60,** 1003–9 (1964).
(7) J. W. S. Hearle, B. M. Chapman, and G. S. Senior, The interpretation of the mechanical properties of wool, *Appl. Polym. Symp.,* **18,** 775–94 (1971).
(8) M. Spei and H. Meichelbeck, X-ray diffraction studies on reduced and reduced-extended fibers, *Colloid and Polym. Sci.,* **254,** 348–55 (1976).
(9) A. Katchalsky and I. Micheali, *J. Polym. Sci.,* **15,** 69–86 (1953).
(10) M. M. Breuer, The stress-strain isotherm of keratin fibers, *Biopolymers,* **6,** 1053–4 (1968).
(11) D. Rosen, Dielectric properties of protein powders with absorbed water, *Trans Faraday Soc.,* **59,** 2178–90 (1963).
(12) P. Alexander and R. F. Hudson, *Wool Chemistry and Physics,* Reinhold Publ. Co., New York, Pp. 180–221, 1954.
(13) M. M. Breuer, The hydration of hair and the effect of water on the mechanical properties of hair, *J. Soc. Cosmet. Chem.,* **23,** 447–70 (1972).
(14) M. Feughelman and J. W. Snaith, *Biochem. and Biophys. Acta,* **79,** 203–5 (1964).
(15) G. Heidemann and H. Halboth, The swelling of collagen in alcohols, *Textile Res. J.,* **40,** 861–2 (1970).
(16) T. H. Nemetschek, The effect of crosslinking on the swelling behavior of collagen, *Zeitsch. Kolloide Polym.,* **55,** 55–7 (1971).
(17) L. J. Wolfram and B. Milligan, Noncovalent bonding in keratin, *Proceedings of the 5th International Wool Conference, Aachen,* Volume III, 242–251 (1975).