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The Swelling of Hair and a Viscose Rayon Monofil in Aqueous Solutions*

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Abstract

Equipment for measuring the swelling of nearly round single fibers in a variety of solutions is described and has been used to make measurements on the swelling of human hair and a viscose rayon monofil. In particular, measurements have been made on the swelling of both types of fiber in various alkali halide solutions and of the hair in HCl solutions. Except for NaCl solutions, the solutions used in this work caused swelling beyond that caused by liquid water, indicating that the solutes were absorbed by the fibers.

The results using LiCl and LiBr solutions are noteworthy in that considerably more swelling occurs in these solutions than in water. The increase in swelling over the water-swollen value is about 25% in the case of hair and 60% in the case of rayon. The high degrees of swelling of hair must be reached by successive replacement with increasingly concentrated solutions, direct immersion of a water-swollen hair into a concentrated solution causing deswelling. For the viscose rayon, either method causes similar swelling.

The swelling changes in hair caused by altering the different variables common in an acid dye bath for wool have also been studied.

Introduction

When a hydrophilic fiber which has been brought to equilibrium with liquid water is immersed in an aqueous solution, the normal swelling which results from the immersion of the fiber in water is usually changed. The degree of swelling and its change with the concentration of the solution give information on the interaction between the fiber and the solute of the solution. For example, if the fiber is impermeable to the solute, a decrease in swelling is to be expected because of the lowering of the vapor pressure of water by the solute. On the other hand, if the solute itself is absorbed appreciably, this decrease in swelling can be overbalanced by an increase resulting from the absorbed solute with an over-all increase in swelling as the net result. Osmotic absorption of water is also possible if ions are absorbed by the fiber. Finally, if the water within the fiber fills a system of micropores and the solute is not specifically absorbed by the fiber, the solution will fill the micropores without change in volume of the fiber.

Some results on the swelling of human hair and of a viscose rayon monofil are given in this paper. Direct microscopic measurements of the swelling were made. Since the work was undertaken as part of a program on dyeing, most of the experiments were related to various aspects of dyeing procedures.

In the acid dyeing of keratin fibers, of which human hair is an example, there are four factors which can influence the swelling—namely, the pH, the dye, the added salt, and the temperature. Results are

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given on the effect of pH and temperature separately on the swelling of hair and on the swelling in one representative dye bath. Swelling in several alkali halide solutions has also been studied.

The swelling of the viscose monofil has been studied less extensively. Results are shown for several alkali halide solutions.

Experimental

The swelling measurements were made microscopically in a small cell designed to operate at temperatures up to 90°C, and to be inert to strong acids up to about 1*N* and to concentrated salt solutions.

Apparatus

The microscope cell is shown in Figure 1. The main body of the cell is made of a cotton-impregnated phenol formaldehyde resin called "Textolite." The jig and the inlet and outlet nipples are made of 303 stainless steel. All other metal parts which do not come in contact with the immersion liquids are brass, except for a phosphor-bronze spring provided to keep the fiber under a slight tension. The windows of the cell are 24 × 50 mm. cover slides and are cemented in with a phenolic resin varnish, Bakelite type (BJ-16320), a viscous partially polymerized resin which sets on exposure to air to make a waterproof seal. The cement is soluble in alcohol and ether so that the cell should not be used, in general, with organic liquids.

The cell is used in a vertical position. The jig is made from a cylindrical rod and is conical at the bottom. The point of the jig fits into a conical slot in the cell to ensure reproducible alignment of the jig in the cell. The jig has a small screw clamp just above the conical point to hold the fiber. The spring also has a small screw clamp to hold the upper end

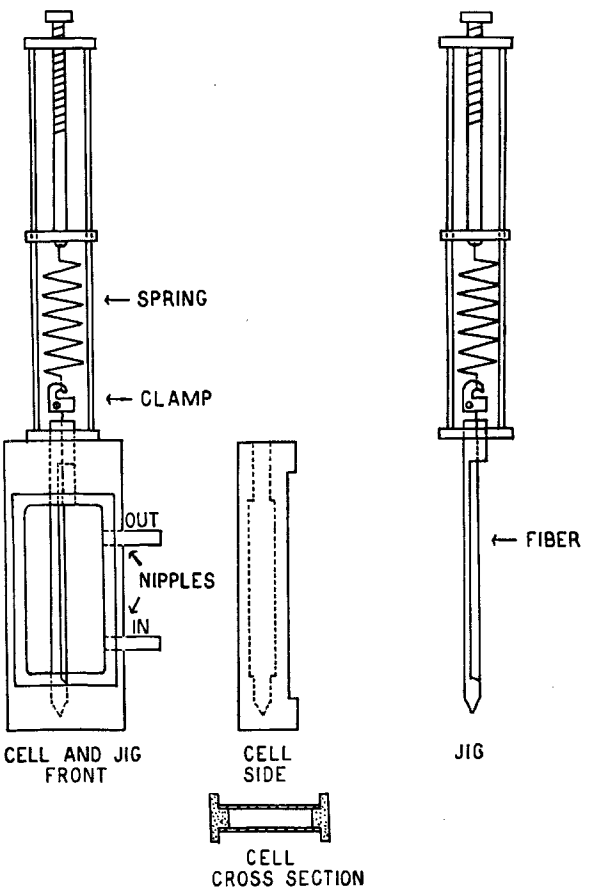

FIG. 1. *Apparatus for measuring fiber swelling microscopically.*

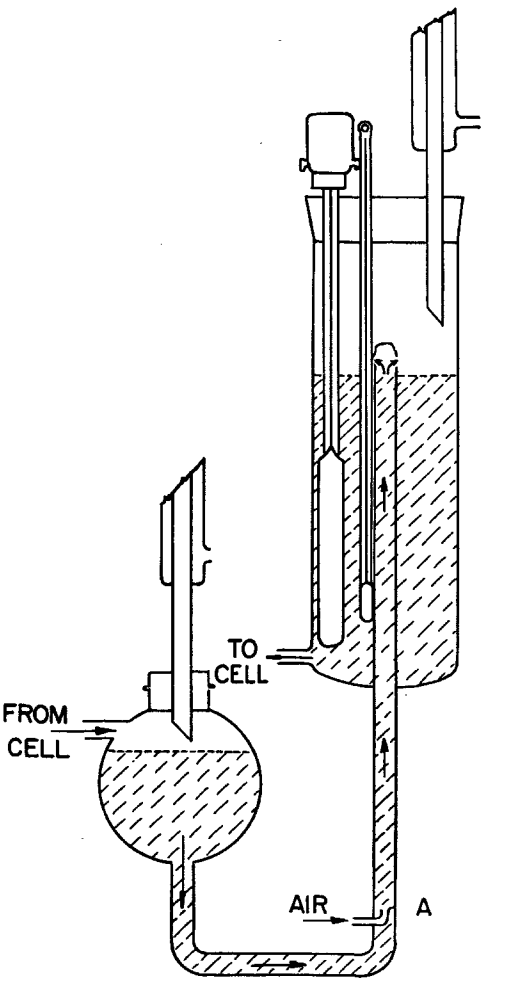

FIG. 2. *Flow system for use with microscope cell.*

of the fiber. Slightly more than three-quarters of the central portion of the jig is cut away, leaving a little less than a quadrant of the rod in the region in which the fiber is mounted. The fiber is mounted as closely as possible to the axis of the jig. Using this arrangement, two profiles of the fiber 90° apart can be made visible in the microscope by turning the jig. Stops (not shown in Figure 1) are provided on the top of the cell to ensure two reproducible settings of the jig, and hence two reproducible profiles of the fiber. If care is taken in making the jig, the fiber can be positioned 1 or 2 mm. from the top cover slide for either profile, and thus a 21 × objective having a working distance of 8 mm. can be used. The other dimensions of the cell and jig are not critical. The rotation of the fiber is necessary because fibers are usually not circular in cross section.

For most of the measurements the cell was simply filled with liquid at room temperature. For cases in which temperature control was desired, the flow system shown in Figure 2 was employed. The flow system is a simplified version of that used in the "dyeometer" [9]. The main reservoir is wound with two 22-ohm Chromel wire coils. One coil is connected across the output of a Variac and set to keep the bath a degree or so below the desired temperature. The other is controlled by the thermoregulator which is immersed in the main reservoir. A temperature control of a few tenths of a degree at 90°C is obtained. Condensers prevent evaporation. Flow through the cell into the overflow reservoir occurs because of gravity. The return flow is provided by the jet of gas introduced at *A*.

Preparation of Materials

All samples of hair used were taken from a single head of blonde hair, and only unmedullated hairs were used.* The hairs had an average diameter of 50 μ and were selected to minimize ellipticity. This was done to increase the accuracy with which the cross-sectional area could be measured using two profiles 90° apart. The diameter was determined at three angles at frequent intervals along the hair. If the ellipticity in percent is defined by

$$200\left(\frac{a-b}{a+b}\right),$$

where a is the largest diameter measured at a position along the fiber and b the smallest, the fiber was accepted only if the ellipticity was uniformly less than 10%.

The hairs were washed in water, extracted with methyl alcohol, ether, and methyl alcohol again. The extractions were of at least one hour's duration. The extracted fibers were then washed with water for several hours at room temperature. No preliminary buffering or special dialyzing was used.

The viscose rayon used in these experiments was an experimental monofil of about 65 μ average diameter, with an average ellipticity of less than 4%, and essentially without bulges or taper.†

The viscose was extracted and washed by the techniques used with hair, and mounted on the jig.

The salts used were reagent grade except for the LiCl and LiBr. These were obtained in a technical grade. They were purified by solution, treatment with activated carbon, filtration, and finally recrystallization. For all salts, saturated solutions were made and diluted to the appropriate concentration. The exact concentrations of the LiBr solutions were determined by analysis of the halide content by titration with silver nitrate using fluorescein as an indicator. For the other salts, solubility values taken from the literature were used to determine the concentration.

The acid solutions were made up using a pH meter for solutions of pH greater than 1. The concentrations of the solutions of lower pH were determined by titration, with one exception as noted.

Procedure

The microscope was used with the barrel horizontal. The cell was fastened to the movable stage of the microscope in such a way that it could be moved up and down. The vertical position of the stage could be determined from a vernier scale which was helpful in reproducing settings. A 21 × objective and filar micrometer eyepiece were used, giving a total magnification of 260 ×.

The fiber was mounted on the jig, and two or three dabs of resin cement were dried to it to serve as reference points. After the jig was fitted into the cell, the cell was filled with water, and 24 hrs. were allowed for equilibrium swelling to be reached. The fiber diameter was read at 15 points about 0.5–1.0

* These samples were obtained through the courtesy of the Friez Instrument Division, Bendix Aviation Corporation, Towson, Md.

† The sample was obtained through the courtesy of Dr. A. C. Walker of Bell Telephone Laboratories, Murray Hill, N. J.

mm. apart. The points were chosen with reference to some distinctive feature of the hair's profile. The vernier setting plus a rough sketch of the relationship of the points to the distinctive surface feature of the hair enabled the same point to be found again for the next set of readings. The process was then repeated at the same intervals for the other profile. In this way, 15 cross sections of the fiber were selected and measured for each set of experimental conditions. Since variations along the fiber are often large compared to changes resulting from changes in the experimental conditions, it was necessary to compare the same cross sections as much as possible to minimize errors resulting from tapering or bulging of the fiber. The relation of the surface features to the permanent reference marks was noted in case one of the features was lost.

Each set of 15 points was measured twice, and the sums of the apparent diameters were taken. The readings were rechecked if the repeat sums varied by more than 0.1% An average diameter was determined for each profile, and the two average diameters were substituted into the formula for the area of an ellipse to determine the average cross-sectional area. The use of any two orthogonal diameters of an ellipse of ellipticity less than 10% introduces an error of less than 0.5% in the area of the ellipse. The statistical standard error of the mean for any one average area was about ± 0.5% [1, 15, 21].

Length changes were easier to measure. The length between two of the fiducial marks on the hair was measured. Since the marks could be as much as 10 cm. apart, a considerable degree of precision could be obtained. However, it was found that in all the solutions studied the length changes made a negligible contribution to the total volume change, and they were not recorded. (It should be remembered that the water-swollen state was used as a reference state.)*

All measurements were made at room temperature (~ 22°C) except where noted. The solutions were changed occasionally during treatment of the fibers to ensure that the concentration of the solution was not appreciably altered by the fiber or by remnants of previous solutions. The bath-to-fiber ratio was, of course, very large. A minimum of 24 hrs. was allowed for equilibrium. This was considered to be adequate from preliminary experiments (see discussion of results, however).

Results and Discussion

Swelling of Hair in Alkali Halide Solutions

The results are reported as percentage increase in volume over the volume of the water-swollen fiber.

* It was pointed out by the reviewer that supercontraction of hair might be expected in some solutions, for example, in concentrated LiBr solutions. (P. Alexander, *Ann. N. Y. Acad. Sci.* **53**, 653 (1951), found supercontraction of wool in LiBr solutions.) No supercontraction was found. As may be seen in Figure 1, our fibers are fastened at both ends and would be forced to extend a spring if they contracted. The spring was weak, but it is within the realm of possibility that its retarding action was sufficient to reduce supercontraction to a negligible amount.

TABLE I. SWELLING OF HAIR IN NaBr SOLUTIONS

Fraction of saturation	Concentration (mol./1000 g. water)	$[(V-V_w)/V_w]\times 100$ Hair #1	Hair #2
0.1	0.7	—	1.9
0.2	1.5	1.7	2.4
0.4	3.2	4.0	3.5
0.6	5.1	4.5	3.5
0.8	7.0	4.0	3.2
1.0	9.1	3.8	3.0

TABLE II. SWELLING OF HAIR IN LiCl SOLUTIONS

Fraction of saturation	Concentration (mol./1000 g. water)	$[(V-V_w)/V_w]\times 100$ Hair #1	Hair #2
0.1	1.4	11.3	4.2
0.2	2.8	11.2	5.8
0.4	6.2	—	6.4
0.5	8.1	14.1	—
0.6	10.1	—	10.5
0.8	14.3	23.3	10.5
1.0	19.5	25.0	9.4

TABLE III. SWELLING OF HAIR IN LiBr SOLUTIONS

Approximate fraction of saturation	Concentration (mol./1000 g. water)	$[(V-V_w)/V_w]\times 100$ Hair #1	Hair #2	Hair #3
0.1	1.2	—	2.6	—
0.2	2.6	—	4.5	—
0.4	5.7	7.6	7.1	4.1
0.6	9.0	—	23.0	16.7
0.8	13.0	—	26.9	22.7
1.0	17.7	30.1	28.8	23.6
water	0	7.1	7.9	5.6

As a reference, Stam [15, 16] found an average value of 32 ± 1% for the increase in volume of a hair on being transferred from the dry state to liquid water. The concentrations of the salt solutions are given as mol./1000 g. water, *m* (molality). The molarity obtained from analysis of the solutions or from the solubility was converted to molality with the use of density values taken from the International Critical Tables. The dependence of the equilibrium swelling on salt concentrations was found to be the following:

NaCl—No change in the water-swollen dimensions was found for a hair in NaCl solutions. (In view of the results using other alkali halides, these results should be checked.)

KI—A 1*m* solution of KI caused a 13.8% increase in volume. Solutions of higher concentrations reacted with the fiber, causing it to break.

NaBr—The swelling of two hairs in NaBr solutions is shown in Table I.

LiCl—The swelling of two hairs in LiCl solutions is shown in Table II.

LiBr—The swelling of three hairs in LiBr solutions is shown in Table III.

The results in Tables I and III are plotted in Figure 3. It is evident that the swelling power of LiBr is much greater than that of NaBr, although the two are comparable over most of the concentration range in which they overlap. It should be remembered that zero on the swelling axis corresponds to the water-swollen fiber. The greatest swelling shown in LiBr solutions corresponds to about 70%, based on the dry volume of the fiber.

The agreement between fibers for the swelling in LiCl and LiBr solutions is poor. Two causes possibly contributing to the discrepancies between fibers can be mentioned. In the first place, the water-swollen cross-sectional areas of the fibers used in the experiment with LiCl solutions are in the ratio 1 : 1.58, and those in the experiment with LiBr solutions in the ratio 1 : 1.26 : 1.46. The degrees of swelling decrease in the same order. It is thus possible that the finer fibers swell proportionately more. It is also known now that the absorption of LiBr from concentrated LiBr solutions is slow, as will be discussed in a future paper. It seems probable that the 24-hour swelling period is insufficient in a LiCl or LiBr solution at a concentration of 0.6 saturation or above. If equilibrium has not been obtained, it is to be expected that the drop below the equilibrium value will be most pronounced with the thickest fibers.

The results in Tables II and III have been taken by bringing the hair to equilibrium with dilute solutions of the respective salts, and then replacing these with successively more concentrated solutions.

When a water-swollen hair was immersed directly in a saturated LiCl solution, a 22.5% decrease in the cross-sectional area of the hair was found. (Drying of a water-swollen hair causes a decrease of about 25.6%.) The area of the hair was about the same as the area that would be found with a hair suspended over the LiCl solution (relative humidity 11.6%). Thus, immersion directly into a saturated LiCl solution apparently dries the fiber out, while the replacement technique causes increased swelling. This same phenomenon occurs with LiBr, and some further information on this effect can be obtained from Figure 4, which shows the volume change of a water-

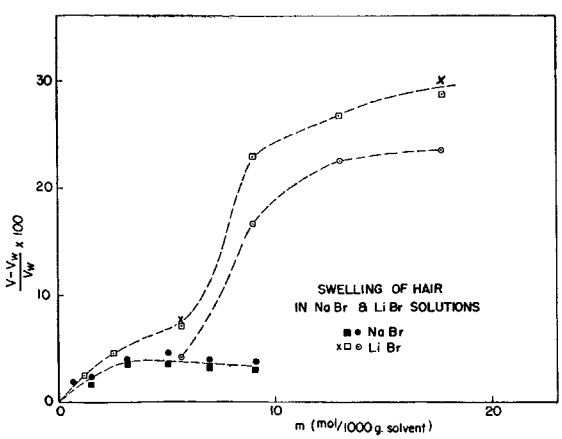

FIG. 3. *Swelling of hair in NaBr and LiBr solutions.*

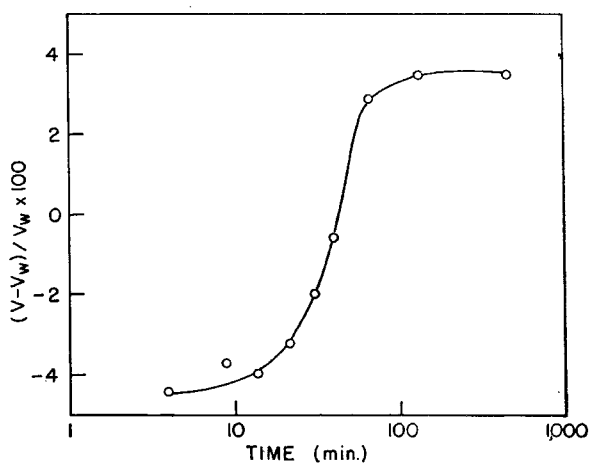

FIG. 4. *Rate of swelling of hair on transfer from water to a 5.7*m *LiBr solution.*

swollen hair immersed directly in a 5.7*m* LiBr solution as a function of time. At zero time the fiber is at zero on the ordinate. Thus, there is first a decrease in volume, and finally an increase. The behavior in LiBr or LiCl solutions can be explained in the following way.

When a water-swollen hair is immersed in a LiBr solution, water starts to diffuse out of the fiber, and salt to diffuse into it. The rate of diffusion of the salt is slower than that of the water and becomes slower as water is removed from the fiber. In a very concentrated solution so much water is removed from the fiber that the rate of diffusion of salt into it becomes infinitely slow, and the fiber is, in effect, dehydrated. In less concentrated solutions, the two opposing rates produce a minimum in the curve of swelling against time. These results were predicted by Burte [3] from consideration of experiments on the mechanical properties of hairs in salt solutions. Other measurements on the effect of LiBr solutions on the physical properties of hair have been reported by Hambraeus and Steele [5] and Steele [17]. In particular, Hambraeus and Steele found that the crystalline x-ray pattern of hair was destroyed by concentrated LiBr solutions when the hair was brought to equilibrium with the LiBr solution by the replacement technique.

The last row in Table III gives the swelling increases for hairs which have been transferred from saturated LiBr solutions to water. Hair #2 was left in water for five weeks. The rate of swelling recovery of hair #3 is shown in Figure 5. The initial degree of swelling is shown by the dotted line. A fairly rapid partial recovery is made, but a marked hysteresis of roughly 25% remains after a week in water.

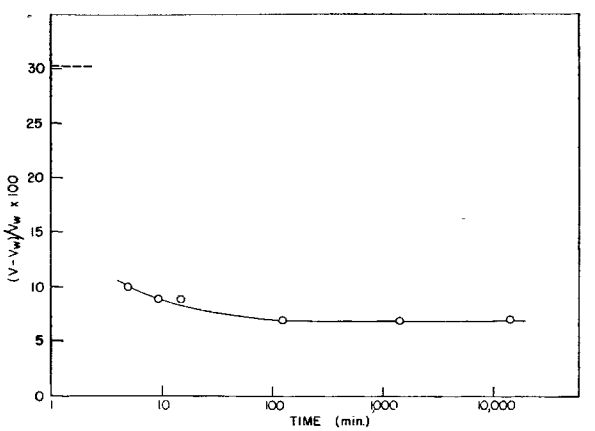

FIG. 5. *Rate of swelling recovery of hair on transfer from a saturated LiBr solution to water.*

Swelling of Hair in HCl

In Table IV and Figure 6 results are given for the swelling of hair in HCl solutions as a function of the pH of the solution. The pH values have been measured by means of a pH meter over the entire concentration range for hair #1 and down to pH 1 for the other hairs. The concentrations of the more acid solutions in the case of the other hairs were determined by titration. The pH values reported are negative logarithms of hydrogen ion concentration rather than pH-meter readings for the more acid

TABLE IV. SWELLING OF HUMAN HAIR IN HCl SOLUTIONS AT ROOM TEMPERATURE

	$[(V-V_w)/V_w]\times 100$			
pH	Hair #1	Hair #2	Hair #3	Hair #4
4.5	0.6			
4.0			0.3	0.8
3.4	1.8			
3.0			0.7	1.9
2.5	1.5			
2.0	2.1		2.0 2.5	3.1
1.5	4.4			
1.0	5.4	2.9	3.6 3.8	4.1
0.51		2.1	2.3	2.8
0.45	5.9			
0.27		1.7	1.2	2.4
0.17	5.0			
0.00		2.1	0.8	2.3
−0.12	5.8			
1.0		3.1	3.6	
H_2O			0.0 0.2	

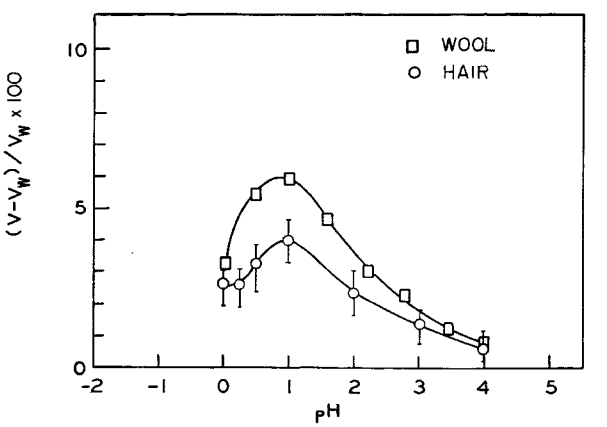

FIG. 6. *The swelling of keratin fibers in HCl solutions at room temperature. (The data for wool are from Speakman and Stott [14].)*

solutions. Below pH 1 there is a slight difference between the two, and the pertinent results for hair *#1* contain a small correction [19]. The maximum correction is about 0.1 pH unit.

The results in Table IV were taken chronologically from top to bottom. Thus the last two rows represent desorption experiments and show that no swelling hysteresis occurs within the concentration limits set. The last row shows results in distilled water. The experiments in the second column for hair *#3* followed those in the first.

An average curve of pH against swelling for the four hairs is given in Figure 6. Because of the differences between individual fibers and the shape of the pH-swelling curve, the curve shown can be taken to apply to pH measurements made with a pH meter with negligible increase in error. The second curve in Figure 6 shows results obtained by Speakman and Stott [14] for the swelling of wool in HCl solutions. A different microscopic technique was used, and the pH was determined with a pH meter. A measurement by Bogaty, Sookne, and Harris [2] on wool at pH 1 falls on the curve obtained by Speakman and Stott.

The difference between the curves for hair and for wool in the low pH region is somewhat surprising in view of the close chemical similarity between the two. Speakman and Elliott [13] found hair to absorb roughly 7% less HCl than wool from a solution of pH 2. However, this small decrease would not be expected to cause such a large decrease in swelling.

The cause of the increase in swelling above that of the water-swollen fiber can be examined by means of the following approximate calculation. Since the relative humidity of a 0.1*N* HCl solution differs negligibly from that of water, the amount of water in the fiber can be set provisionally equal to the regain over liquid water. Thus for a hair (or wool fiber) in a 0.1*N* HCl solution, the amount of water present within the fiber is 0.31 g./g. [4], and the amount of acid 0.8*mM*/g. [18]. The molarity of the "acid solution" in the hair is thus 2.45 mol./l. [6]. The apparent molal volume of HCl in water solutions, which is the increase per mole of acid added of the volume of the water phase on forming the solution, is given by the equation [7]:

$$\phi_V = 18.2 + 0.83\ C^{1/2},$$

which applies, strictly speaking, to more dilute solutions but should be accurate to the approximation desired here.

For a 2.45*M* solution, this is 0.020 cc./*mM* or 0.016 cc./g. dry fiber. This is the increase in volume per g. dry fiber to be expected when a water-wet fiber is transferred to a 0.1*N* HCl solution. Since the density of dry wool (and presumably hair) is 1.31 g./cc. [10] and the volume increases by 1.31 : 1 on wetting [15], this is also $(V-V_W)/V_W$. The actual values, as seen from Figure 6, are 0.061 for wool and 0.04 for hair.

This calculation assumes that the HCl causes the same volume increase within the fiber that it causes in aqueous solution. The equation above shows that in aqueous solution the apparent molal volume is relatively insensitive to concentration changes and hence to small changes in environment. It seems unlikely that the apparent molal volume would increase two- or threefold in the hair. In fact, by analogy with water and other absorbates, a slight decrease in apparent molal volume might be expected. Thus, the discrepancy between the calculated and measured swelling values probably results from the assumption that the hair contains the same amount of water as in the water-swollen state. If more water is absorbed, either because of osmotic effects, as discussed by Procter and Wilson [11], or because the absorption of acid reduces the cohesive forces of the hair which resist swelling, the discrepancy is explained. Since most of the swelling is caused by water rather than by absorbed acid, it is possible for wool and hair to have different degrees of swelling for substantially the same acid content if the forces resisting swelling are different. Such a difference could result from different amounts of crystallinity or differences in morphology.*

TABLE V. SWELLING OF HAIR IN WATER AS A FUNCTION OF TEMPERATURE

Temperature (°C)	$[(V-V_w)/V_w]\times 100$
40	−0.2
50	−0.4
67	−0.6
78	−0.6
93	−0.8
93 (2 days later)	−0.9

* The reviewer noted that the cystine content of hair is greater than that of wool and that the resulting increase in concentration of sulfur cross-links would make hair more resistant to swelling. We agree that the increased cystine content is probably an important factor in explaining the lower swelling of hair. J. M. Lang and C. C. Lucas, *Biochem. J.* **52**, 84 (1952), give the cystine content of hair

Effect of Temperature on the Swelling of Hair in Water

In Table V some results are given on the effect of temperature on the swelling of hair in water. Speakman [12] examined the temperature dependence of the regain for wool. The regain decreases with increasing temperature at low relative humidities. At 95% R.H. a minimum is noted in the curve of regain against temperature at 45°C, the regain being about 7% lower than the regain at 25°C. Also, Speakman found that decomposition of the wool becomes appreciable at 50°C and above. The results in Table V show substantially no effect of temperature on the swelling of hair in water. No large changes in swelling occur with increased treatment at 93°C; however, swelling would not be expected to be a particularly sensitive measure of degradation. Since the measurements were made consecutively from top to bottom, it is possible that hysteresis in swelling recovery such as is found during solvent replacement masks a minimum which might be found by separate swelling experiments at 25°C and 50°C.

as 18.0 g. amino acid/100 g. protein; S. R. Hoover, E. L. Kokes, and R. F. Peterson (TEXTILE RESEARCH JOURNAL 7, 423 (1948)) give the cystine content of wool as 12.72 g. amino acid/100 g. protein.

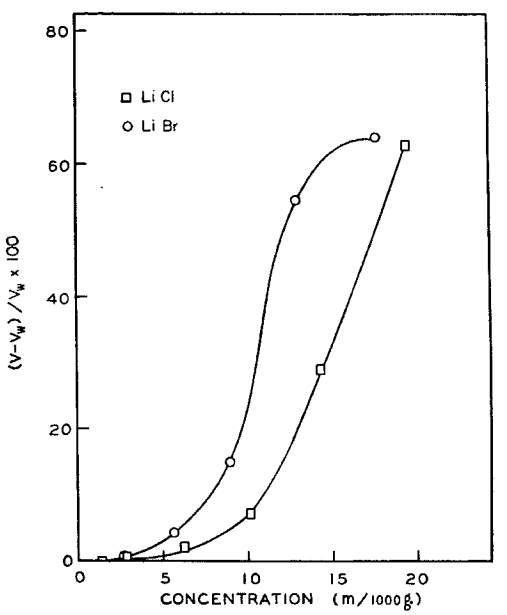

FIG. 7. *Swelling of rayon in LiCl and LiBr solutions at room temperature.*

Swelling of Hair in a Dye Bath

Finally, measurements were taken on the swelling of hair in a typical acid dye bath. The results are shown in Table VI. The first column runs chronologically from top to bottom. At each step one variable was changed until the final solution, which was a typical acid dye bath, was obtained. The dye used was Anthraquinone Blue SKY, Color Index Number 1088.

Swelling of Cellulose

The swelling of cellulose, regenerated by the viscose process, in aqueous salt solutions has been discussed by Usher and Wahbi [20] and by Kasbekar and Neale [8]. These workers used swelling to mean gross weight increase of treated sheets of cellophane rather than the volume change accompanying the increase. Since, in both cases, the composition of the cellulose phase was analyzed completely, the volume change of the cellulose could be calculated to a fair degree of accuracy by assuming appropriate partial molal volumes for the various absorbed components. However, since these workers used different salts and a different form of cellulose than were used for the work described herein, such a calculation for comparative purposes was not made.

The swelling which resulted when a dry viscose monofil was equilibrated with liquid water was determined to give some degree of characterization of

TABLE VI. SWELLING OF HAIR IN A DYE BATH

History	$[(V-V_w)/V_w]\times 100$
pH 2, room temperature	2.1
pH 2, 95°C	2.7
pH 2, 95°C, 0.53 g. NaCl / 400 cc.	3.7
pH 2, 95°C, 0.53 g. NaCl / 400 cc., 0.021 g. dye / 400 cc.	7.4

TABLE VII. SWELLING OF VISCOSE IN LiCl SOLUTIONS

Fraction of saturation	Concentration (mol./1000 g. water)	$[(V-V_w)/V_w]\times 100$ Fiber #1	Fiber #2
0.1	1.4	0.2	—
0.2	2.8	0.7	0.4
0.4	6.2	3.3	0.7
0.6	10.1	8.9	5.5
0.8	14.3	28.5	29.9
1.0	19.5	65.6	60.6

the monofil used. This swelling was measured in the following way. A mounted monofil was dried over magnesium perchlorate in a vacuum desiccator for three days and then quickly removed and put into the cell, while the cell was being flushed with air previously passed through a drying train containing magnesium perchlorate as the last stage. The volume of the monofil was measured under these conditions and considered to be the dry volume. The cell was then filled with water, and after 24 hrs. the volume was measured. The water caused a 75.5% increase in area and a 4.0% increase in length. Subsequent solutions caused no further change in length.

Swelling of Cellulose in Alkali Halide Solutions

NaCl.—As was the case with hair, a saturated solution of NaCl caused the same degree of swelling as water. The same swelling was observed when a dry fiber was put into a saturated solution as when a water-swollen fiber was transferred to a saturated solution.

KI.—A saturated KI solution caused a 12.3% increase in volume over the water-swollen volume. All the increase was radial. When the fiber was washed with water for 24 hrs., 3.3% of the swelling remained, showing a hysteresis in the swelling-deswelling cycle.

LiCl.—The swelling of the viscose monofil in solutions of LiCl at room temperature is shown in Table VII and Figure 7. The curve for LiCl in Figure 7 is an average of the results for the two fibers. The results were obtained in descending order chronologically. However, contradistinct to hair, the same results can be obtained in a reasonable period of time by direct immersion even in very concentrated solutions. In the case of fiber #2, the saturated solution was replaced with water and the cell flushed with water periodically for a week. The swelling recovery was followed as a function of time, and is shown in Figure 8. The initial degree of swelling is shown by the dotted line. As with hair, as shown in Figure 5, a fairly rapid partial recovery is made followed by a slower process with the fiber remaining 10% larger than the water-swollen fiber after a week in water. The shape of the curve of Figure 8 suggests that the secondary recovery process is faster with the viscose monfil than with hair.

TABLE VIII. SWELLING OF VISCOSE IN LIBR SOLUTIONS

Approximate fraction of saturation	Concentration (mol./1000 g. water)	$[(V-V_w)/V_w]\times 100$ Fiber #1	Fiber #2
0.2	2.6	0.8	—
0.4	5.7	4.4	4.4
0.6	9.0	14.8	15.3
0.8	13.0	54.1	55.6
1.0	17.7	63.4	65.0

LiBr.—The swelling of the viscose monofil in LiBr solutions at room temperature is shown in Table VIII and Figure 7. Again the curve in Figure 7 represents an average of the results for the two fibers shown in Table VIII.

The results in Table VIII show that the action of LiBr is quite similar to that of LiCl, with slightly higher swelling at a given concentration occurring in the case of LiBr. As was true with LiCl solutions, the replacement method was not necessary in the case of viscose even when the treating solution was quite concentrated. If a swelling minimum such as is shown in Figure 4 existed, it was passed before it was possible to make the first measurement. Thus there is a basic difference between the hair and the rayon with respect to the rate of swelling, which suggests that the rayon monofil has a more open molecular structure than the hair. Whether this is true for more highly oriented rayons remains to be seen.

Conclusions

It may be concluded from the swelling results reported here that all of the solutions used are absorbed in appreciable quantities by both hair and viscose rayon with the possible exception of NaCl. Here absorption is used to denote any penetration

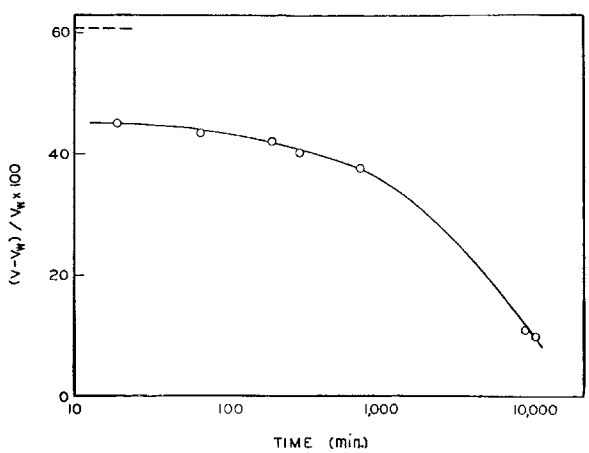

FIG. 8. *Rate of swelling recovery of rayon on transfer from saturated LiCl solution to water.*

within the fiber and not merely differential uptake with respect to water. Further analysis of the nature of the absorption depends on a knowledge of the amounts of water and solute absorbed by the fiber. The case of hair swollen with HCl has been discussed to some extent, and the action of NaBr and LiBr on hair will be treated in a further paper.

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