

Quantification of Human Hair Moisturization with Cosmetic Products by Dynamic Vapor Sorption

Y. K. KAMATH, *Kamath Consulting Inc., Princeton, NJ*

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ABSTRACT

An attempt has been made to evaluate and quantify the moisturizing efficacy of cosmetic products by dynamic vapor sorption method. The possibility of quantifying this effect by the application of the second law of thermodynamics to sorption hysteresis has been demonstrated. The results show that the ordinary conditioner actives in rinse-off formulations show limited moisturizing capabilities. However, specially formulated products can show, quantifiably, both moisturizing and desiccating effects. From the Brunauer, Emmett and Teller (BET) theory, total pore volume obtained from the literature by nitrogen adsorption, and the sorption data from this work, it has been possible to show that the sorbed water in hair does not distribute uniformly in the hair. This is in agreement with the X-ray diffraction measurements and the more recent work on small angle neutron scattering on D₂O-saturated hair.

INTRODUCTION

Mechanical properties of hair such as bending and torsion moduli, which sensitively affect the softness of hair, are governed by its moisture content. An optimally moisturized hair is supposed to be shiny, smooth, and soft to touch and beautiful in appearance. However, drastic changes in the humidity surrounding the hair can change the moisture content with a consequent change in its softness and appearance.

From a material science viewpoint, hair is a unique composite fiber structured from spindle-shaped cells (cortical cells) held together by cell membrane complexes (CMCs) (cortex) and wrapped around by a multilayered sheath of flat cuticle cells (1). Cortical cells themselves are composite cells consisting of rod-like intermediate filaments embedded in an amorphous protein matrix. Included in the cortex are some cells which were left empty without protoplasm, forming the medulla. In thick hair, medulla can be a continuous tube, almost like a capillary. In thinner hair, the medullary channels could be narrow and discontinuous (1, pp. 45–48, 2). Excessive medullary structures can affect the shine of hair (3). These structures in hair may have a special association with water because of their volume and less-keratinous (low cysteine) nature.

Address all correspondence to yashkamath@verizon.net.

The importance of water to hair can be experienced by running one's fingers through the hair in an environment of low humidity (<20% RH). The hair feels coarse and rough to touch and has a "flyaway" effect due to the development of static charges on the surface of hair. On the other hand, hair in an environment of high humidity (>70% RH) has a limp and heavy feel because of interfiber adhesion from the condensed moisture film on the surface. In this communication, we consider the interaction of water with hair in its natural state, or in combination with cosmetic formulations and actives, and grooming processes.

EXPERIMENTAL

MATERIALS

The hair sample used in these experiments was European dark brown hair obtained from DeMeo Brothers of New York. Sodium lauryl sulfate was obtained from Sigma Aldrich. Cosmetic products used in this study were either raw materials or confidential experimental formulations from commercial sources.

METHOD

Because the behavior of a hair assembly depends on its moisture content, which in turn depends on the transport of water vapor in and out of hair, a device suitable for studying the sorption and desorption of water from hair is used in this work. The device is a dynamic vapor sorption (DVS) instrument supplied by Surface Measurement Systems (Allentown, PA). It is a gravimetric device using a microbalance enclosed in a temperature-controlled incubator. The sample pan of the microbalance is enclosed in an environment in which the humidity is controlled with an accuracy of $\pm 0.4\%$, using dry and moisture saturated nitrogen (bubbled through distilled water) in an appropriate proportion with a humidity controller. In this work, all experiments were carried out at 25°C.

In a typical experiment, about 20 mg of hair is placed in the sample pan and the humidity set for 0% RH. The sample is completely dried to a constant weight and the weight is recorded. Then the humidity is increased by steps of 10% up to 95% RH, the last step being 5%. The weight of the sample is recorded at the end of each step when the equilibrium is reached. The attainment of equilibrium is automatically sensed by the instrument based on the dM/dt value set in the software (for hair this value is generally 0.001%/min). If the behavior of the sample is known from previous experiments, then the equilibrium criterion can also be set to a maximum time limit (2–3 h for hair) for each step. Equilibrium is attained in this relatively short time because of the small sample size (20 mg).

Apart from obtaining sorption-desorption (S-D) isotherms, the instrument can also be used to determine moisture contents of materials at a given humidity. It should be noted, however, that with materials which show sorption hysteresis, such as hair, the moisture content at a given humidity depends on whether we approach that humidity from the dry side or the wet side.

THERMODYNAMIC ORIGIN OF SORPTION HYSTERESIS

The following discussion is based on the work of W. P. Bryan (4) on sorption hysteresis. The nature of the DVS experiment lends itself conveniently to thermodynamic analysis. If the sorbent (hair) and the sorbate gas (water vapor) are confined to a cylinder with a piston, then sorption and desorption, respectively, can be carried out by reversibly compressing and expanding the sorbate. If the amount of moisture (sorbate) in the hair is determined and plotted as n (moles) vs $\ln P$ (P = partial pressure of water vapor), then we get the sorption and desorption isotherms. If the sorption and desorption process is reversible, then the sorption–desorption isotherms will be coincident, and the overall work carried out is zero ($W = 0$). On the other hand, if the process is irreversible, then applying the second law of thermodynamics, the compression–expansion path gives a loop. The work that needs to be carried out on the system is given by the area of the loop and will be negative as seen in equation 1:

$$W = \oint p dV = -RT \int_{\ln P_{low}}^{\ln P_0} (n_D - n_S) d \ln P, \tag{1}$$

where R is the gas constant, T absolute temperature, n_D and n_S are moles of sorbate in the sorbent during desorption and sorption, respectively, P_0 is the saturation vapor pressure of the pure sorbate, and P_{low} is the pressure between 0 and P_0 .

$W = -RT$ (area of the constant temperature hysteresis loop).

For this purpose, the isotherm needs to be plotted as (moles of water sorbed) vs $\ln P$.

However, in this work, S-D data are plotted in terms of regain% vs RH. The region surrounded by the isotherms is the hysteresis loop. We have arbitrarily quantified hysteresis H at a given humidity as follows:

$$H = M_D - M_S. \tag{2}$$

To correct for this change, we can express equation (2) as $H = K (M_D - M_S)$. Using H , we can express equation (1) as a finite summation as

$$W = -RT/K \sum H_i (i = 1 \dots n) \tag{3}$$

Equation (3) can be used to interpret moisturizing ability of actives from cosmetic formulations on hair.

Irreversibility of the S-D process also leads to an increase in the entropy of the system given by equation (4).

$$dS = R \int_{\ln P_{low}}^{\ln P_0} (n_D - n_S) d \ln P. \tag{4}$$

$\Delta S = R$ (area of the constant temperature hysteresis loop). Increase in entropy reflects the change in the fiber structure as a result of sorption of water and consequent swelling.

Rosenbaum (5) has examined the applicability of Flory–Huggins polymer solution theory to sorption of water into keratin and has found that the theory agrees with the isotherm only at high vapor pressures. Agreement at lower vapor pressures improves with

the consideration of volume change with sorption of water, something similar to the transition occurring in polymers at the glass transition temperature.

QUANTIFICATION OF MOISTURIZATION

Moisturization as understood in the cosmetic industry can be loosely defined as the ability of a cosmetic product to enhance the retention of water in hair or skin. Because both hair and skin naturally have the ability to retain water to a certain extent without the application of any product, we need to define moisturization with reference to the untreated hair or skin. Change in sorption hysteresis as a result of product application enables us to define a hysteresis ratio of the hair treated with the product to that of the untreated hair. A hysteresis ratio higher than 1 (can be expressed as a percentage) indicates the ability of the product to absorb and retain water ($W_{tr} > W_{untr}$). A ratio lower than 1 indicates that the treatment with the product facilitates evaporation of water from treated hair ($W_{tr} < W_{untr}$). We define this ratio as H_R (hysteresis ratio):

(Area of the hysteresis loop of treated hair in a given RH range/Area of the corresponding loop for untreated hair in the same RH range).

$$H_R = W_{tr}/W_{untr} \quad (5)$$

From equation (2), $H = K(n_D - n_S)$ where K is a constant, then assuming the constants to be the same for treated and untreated hair, and replacing the integrals in equation (1) with finite summation, we can express equation (5) as follows (because all other factors cancel):

$$H_R = W_{tr}/W_{untr} = \sum H_{i,tr} / \sum H_{i,untr} \quad (6)$$

($i = 1 \dots n$), n being the number of RH steps selected over the ΔP interval. $\sum H_i$ is the area of the hysteresis loop in the selected range of RH. From a practical point of view, it is suggested that the higher (70–95% RH) and the lower (0–10% RH) segments of the isotherm should not be included in this calculation. Including these regions in the calculation can skew the result, limiting its usefulness. It is this strong interaction between water and the protein component in the mid-humidity range which gives rise to an increase in entropy and the moisturizing effect.

RESULTS AND DISCUSSION

SORPTION HYSTERESIS

Typical outcome of a DVS experiment conducted at a constant temperature (in this work, all experiments were carried out at 25°C) are a pair of isotherms forming a loop (S-D loop). To check the reproducibility of the measurement, we ran three experiments from a single sample of hair. The average moisture contents in each of the experiments in the S-D mode are given in Table I, and the S-D loops are plotted in Figure 1. The S-D isotherm loops clearly show the accuracy of the instrument and excellent reproducibility of

Table I
Moisture Sorption Data for S–D Isotherms in Figure 1 ($n = 3$)

RH (%)	Average regain %	95%	Average regain %	95%
	sorption	confidence level	desorption	confidence level
0	0	0	0.8	0.72
10	2.8	0.46	5.1	0.29
20	5.4	0.41	7.7	0.17
30	7.5	0.11	9.8	0.21
40	9.3	0.09	11.7	0.21
50	11.0	0.14	13.5	0.25
60	12.7	0.25	15.5	0.29
70	14.6	0.24	17.7	0.29
80	17.6	0.19	20.6	0.19
90	23.4	0.38	25.1	0.25

the sorption data in the entire humidity range, and especially in the 10–60% RH range which is most relevant to the efficacy of cosmetic products. This is a result of small sample mass and small space where experimental conditions such as temperature and humidity can be maintained accurately. This suggests that a single S–D run on a sample may be adequate to obtain reliable data on a well-prepared sample of hair.

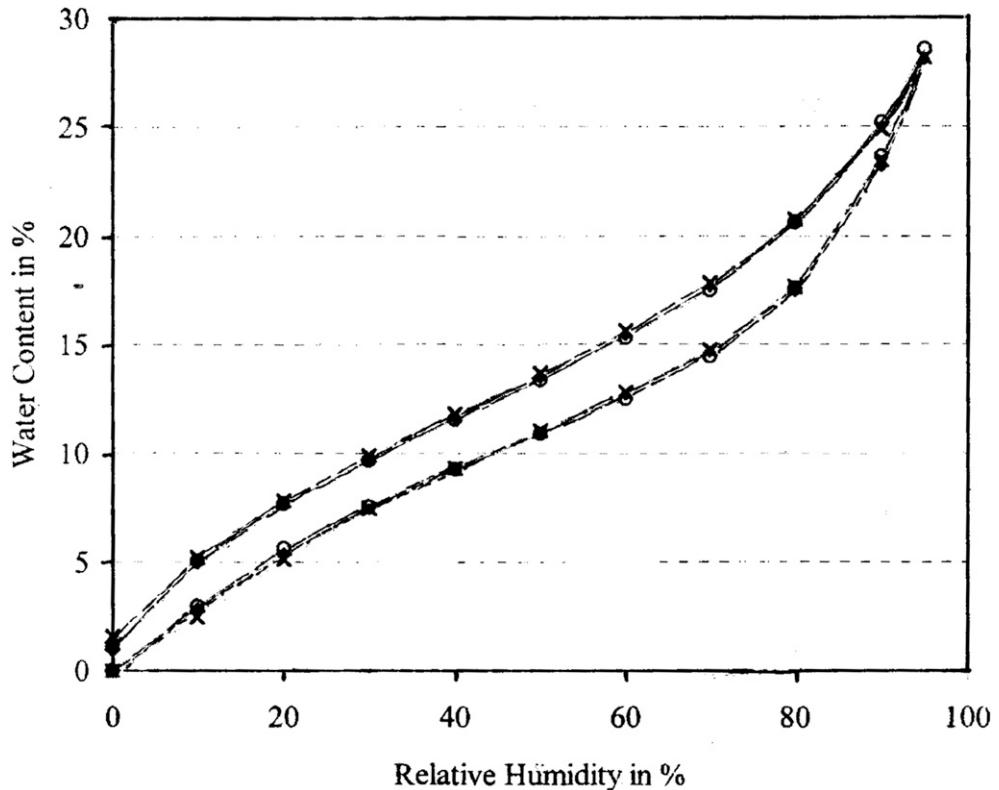


Figure 1. Hair–water S–D isotherms for untreated hair. Expt. 1: ◇; Expt. 2: ○; Expt. 3: x.

EFFECT OF CONDITIONER ACTIVES ON HYSTERESIS

Conditioner actives generally are cationic substances which interact strongly with negatively charged surface of hair. In this preliminary study, we have used three pure conditioning actives, i.e., Polymer JR-400 (Ucare Polymer JR-400, Dow Chemical, Piscataway, NJ), Jaguar C-17 (Rhodia, Bristol, PA), and Rhodaquat [cetyltrimethylammonium bromide (CETAB)]. Depending on their molecular weight, they can adsorb on the surface or penetrate into the hair (6). High molecular weight cationic actives such as polymer JR 400 and Jaguar C-17 essentially deposit on the negatively charged surface of hair and render it hydrophilic. The binding is strong enough to resist removal by simple rinsing (solubilization). On the other hand, low molecular weight cationic actives such as CETAB penetrate the hair in significant amounts and also deposit on the surface of hair by forming salt links with the negative charges of cysteic acid groups, forming a monolayer of C-18 lipid chains and rendering the surface hydrophobic. Rinse-off formulations based on these actives had negligible effect that can be quantified. This was viewed to be due to lack of deposition or penetration of actives.

To ensure adequate deposition of the actives, a rather unconventional method of treatment (compared with normal rinse-off washing) was adopted. The actives were used on hair tresses in their pure form as 0.5% aqueous solutions at 50°C for 10 min followed by five 1-min rinses with distilled water. This treatment was repeated 10 times, after which the tresses were air-dried at 65% RH and 21°C. About 20 mg of hair from each of the tresses was used in the sorption-desorption experiments as described earlier. The sorption-desorption isotherms of hair treated with these conditioners are shown in Figure 2.

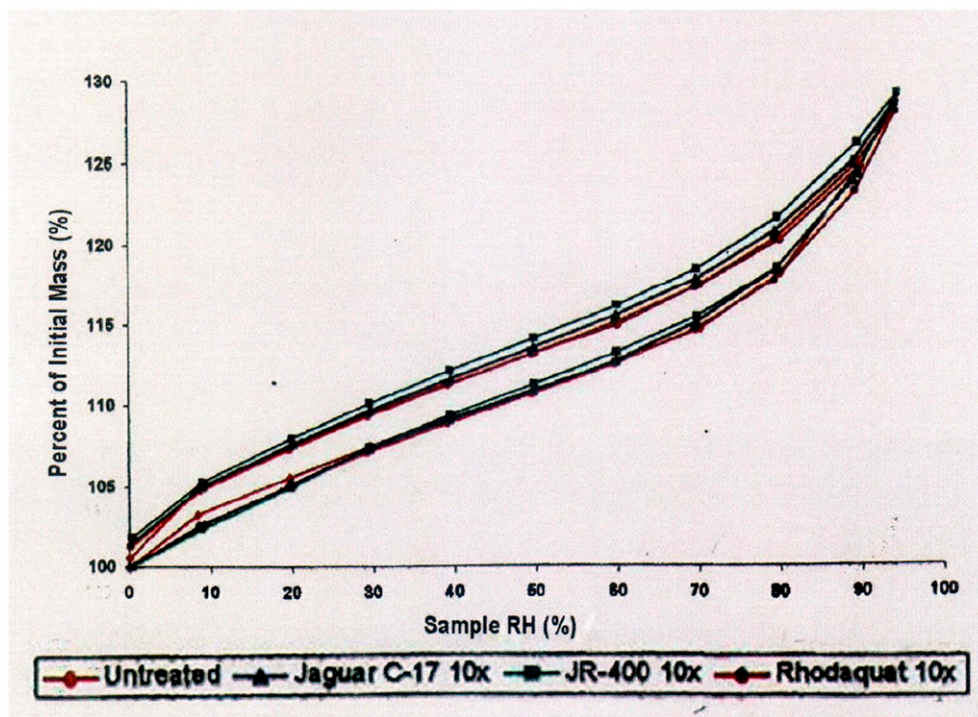


Figure 2. Sorption-desorption isotherms of hair treated with different conditioners.

The sorption–desorption plots in Figure 2 show that the difference in the moisture contents of hair treated with conditioning actives from that of untreated hair is very small (<1%). A closer examination of the S-D isotherms suggests that comparing hysteresis of treated samples with those of the untreated sample at various humidities can provide useful information regarding the moisture retention effect of conditioning actives. Figure 3 shows the hysteresis of hair treated with conditioning actives along with that of untreated hair as a function of relative humidity.

In Figure 3, the hysteresis plot of the untreated hair goes through a maximum at ~70% RH and drops off beyond that value. The hysteresis plots of all conditioner-treated hair fall below that of the untreated in this region of humidity (>70% RH). The plot of polymer JR-400 is higher than all others below 40% RH, indicating it has the best moisture holding capacity at low humidities. Next is Jaguar C-17 below 40% RH. Here, we did an additional experiment with hair treated with Jaguar C-17 only once, and the result is that the plots for both 10X and 1X treatment are virtually coincident. This suggests that with polymeric conditioners which deposit on the surface without penetration, multiple treatments may not have an added effect. All top layers rinse off except the one which is strongly bound to the charged surface. This has been established by repeated wetting force measurements on treated fibers (6). These ionic polymers have the capability of reducing the thermodynamic activity [fugacity (7) and escaping tendency, G. N. Lewis] of water sorbed on/in the hair.

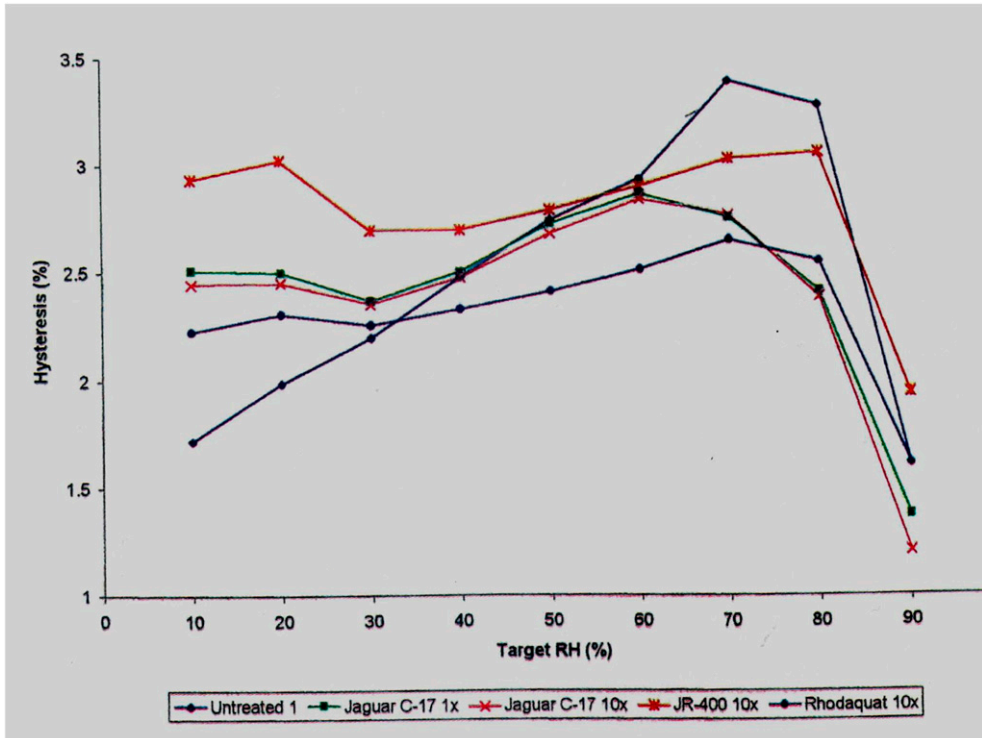


Figure 3. Hysteresis plots of conditioned hair as a function of humidity.

The low molecular weight conditioner CETAB behaves differently. Treatment over long periods of time repeatedly allows for considerable penetration of CETAB into the bulk of hair (8). This increases the hydrophobicity of the cortex, thus limiting the penetration of water molecules into the hair. Because of low interaction with water molecules, they do not retard the diffusion of water out of the hair. Therefore, low molecular weight conditioners have limited moisturizing capability. Hydrophilic polymers, on the other hand, because of their hydrophilicity, even with thin films bound to the surface of hair, and limited penetration into the cuticular zone reduce the evaporation of water. There may be an additional effect of the very low molecular weight component of polymeric actives penetrating into the hair.

HYSTERESIS RATIOS AND MOISTURIZATION

Hysteresis ratios for the plots in Figure 3 for conditioning actives were evaluated according to equation (5) using $i = 1-5$ or $1-9$ to see how the value of i affects the overall H_R . The values are summarized in Table II.

The data in Table II show that if the isotherms are well defined, then even a small value of i yields satisfactory ratios. Values of H_R for 5 and 9 values of i are very close. The values of H_R also show that CETAB is not a good moisturizer, although it gives a very smooth surface by forming a monolayer on the surface of the cuticle cells. The polymers which deposit on the surface (low molecular weight components may penetrate) have a weak moisturizing effect ($H_R > 1$). This is because the moisture associated with the polymer has a lower activity and, therefore, diffuses very slowly from the polymer-fiber composite. JR-400 seems to do better than Jaguar-C-17. CETAB shows a split behavior. Below 30% RH, the value of $H_R = 1.1$, whereas in the range of 30–60% RH, the value of $H_R = 0.92$. Because CETAB penetrates into the fiber (8), the lipid chains packed into the matrix reduce its hydrophilicity and facilitate the release of moisture better than in the untreated fiber. Overall, the data show that the moisturizing effect of ordinary rinse-off conditioners is weak, in spite of multiple

Table II
Hysteresis Ratios of Hair Treated with Conditioning Actives from Figure 3

RH (%)	Hysteresis (%) (H_i)			
	Untreated	CETAB	JR-400	Jaguar C-17
20	1.98	2.32	3.03	2.47
25	2.08	2.29	2.84	2.42
30	2.19	2.26	2.68	2.37
35	2.34	2.29	2.68	2.47
40	2.45	2.32	2.68	2.47
45	2.63	2.37	2.73	2.58
50	2.74	2.42	2.79	2.68
55	2.84	2.45	2.82	2.76
60	2.92	2.50	2.87	2.84
H_R (1-5)	1.00	0.96	1.14	1.04
H_R (1-9)	1.00	0.96	1.13	1.04

H_R (1-5) is for RH 20, 30, 40, 50, and 60. H_R (1-9) is for 20, 25, 30, ..., 60.

treatments. Single treatment with regular rinse-off products is unlikely to have a significant moisturizing effect (there may be other beneficial effects from emollients, similar to the plasticizing effect of water).

EFFECT OF HEAT TREATMENT ON S-D HYSTERESIS OF HAIR

Heat treatment (blow-drying or flat ironing) is a common grooming process used mainly to dry wet hair, and sometimes straighten hair from its curly or frizzy state. The temperatures and the devices used vary, but the overall effect is one of reducing the post-drying water uptake (the amount depends on the temperature and time) which helps prevent curl reversal and reduce frizziness. Covalent cross-linking of hair is possible at relatively high temperatures ($>100^{\circ}\text{C}$) by dehydration reactions involving reactive side groups of amino acids, such as $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$ groups. Because all the three groups are centers for hydrogen bonding, their elimination by cross-linking reduces the amount of water sorbed by hair. Since sorption and desorption occur by diffusion, cross-linking hair reduces the rate of diffusion by increasing tortuosity. In this work, we selected a heat treatment temperature of 120°C for 1 h. This was performed to intensify the effect. The S-D isotherms of untreated and heat-treated (1 h at 120°C) hair are shown in Figure 4.

From the isotherms, we can see that the heat-treated hair absorbs significantly less water compared with the untreated. The ratio of the areas of the hysteresis loops of heat-treated hair to that of untreated hair is 1.45. The hysteresis plots are shown in Figure 5.

From Figures 4 and 5, it is easy to see that heating hair at elevated temperatures reduces the amount of moisture sorbed by the hair; however, it also helps retain that water in hair

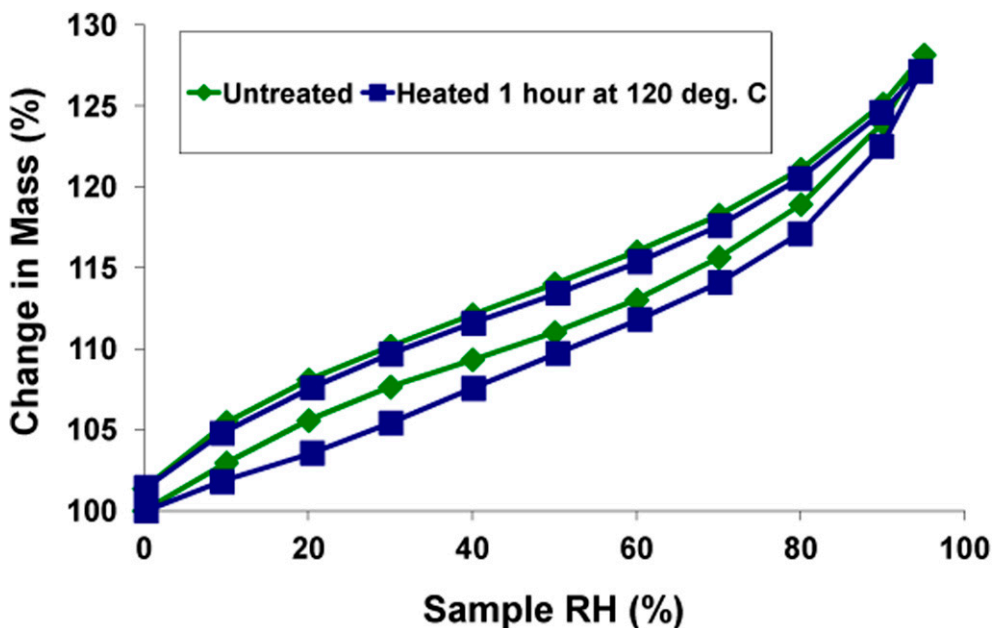


Figure 4. S-D isotherms of untreated and heat-treated hair.

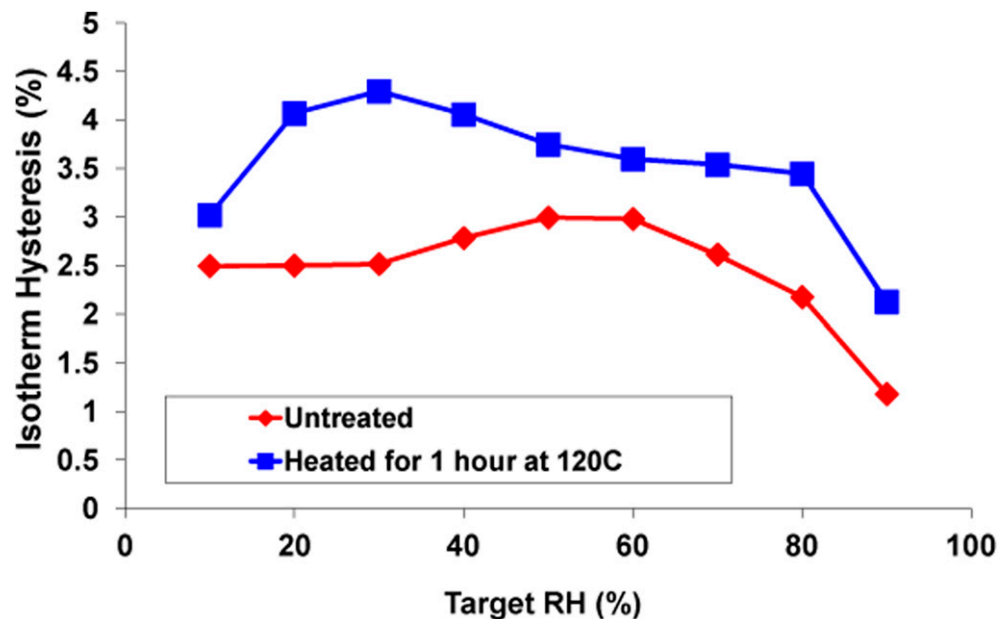


Figure 5. Hysteresis plots of heat-treated and untreated hair.

during desorption. Lower diffusion rate should have no effect on the amount of water retained because desorption is carried to equilibrium. Therefore, higher water contents in the desorption phase suggest that cross-linking generates additional areas in the matrix where water is “locked-in” by cross-links.

WATER DIFFUSION IN HEAT-TREATED HAIR

A unique advantage of a DVS experiment is that it provides a mass change plot as a function of time at a chosen RH. Such a plot can be changed to a plot of M_t/M_{eq} vs \sqrt{t} . From the initial rate of this plot, we can calculate the diffusion coefficient D (9) assuming an average fiber diameter. A plot of diffusion coefficient as a function of RH is shown in Figure 6 for the untreated and heat-treated hair. The diffusion coefficients show a maximum in the mid-humidity range with minima at the extremes, suggesting a transition in the diffusion behavior of water in hair. A possible mechanism for this behavior has been discussed by Keis et al. (9). The lower diffusion coefficients of heat-treated hair compared with untreated hair during both sorption and desorption clearly suggests heat-activated cross-linking of proteins via residual side chain functionalities of amino acids. This is also the cause of higher hysteresis compared with that of the untreated hair. The fact that in the mid-humidity range water retention is higher in spite of higher diffusion coefficients suggests that the diffusion rate alone is not related to hysteresis.

Kinetics of water vapor diffusion in hair is controlled by thermodynamic activity and the tortuosity of the diffusion path. The diffusion of water molecules follows random walk kinetics (10). Based on this concept, we can calculate the distance penetrated by a single water molecule by the equation: $x^2 = 2Dt$, where x is the distance penetrated, D is the

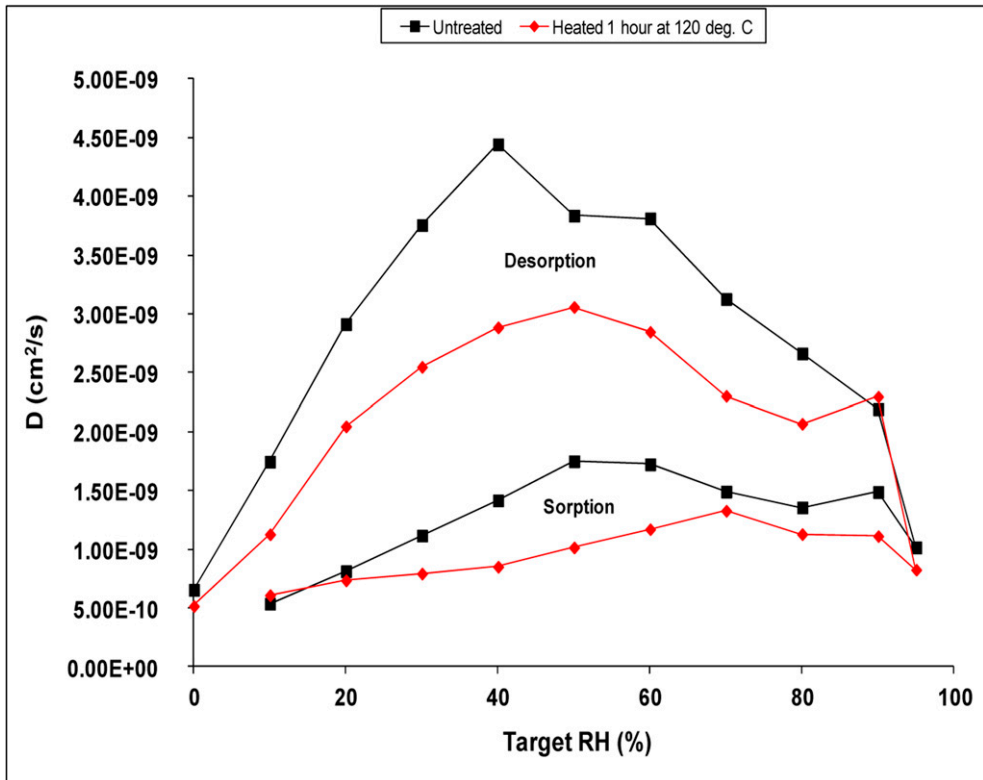


Figure 6. Sorption and desorption diffusion coefficients of heat-treated and untreated hair.

diffusion coefficient, and t is time. For example, the time taken for a water molecule to reach the center of a 100- μm hair at 40% RH and 25°C ($D = 4.5 \times 10^{-9} \text{ cm}^2/\text{s}$) will be 2,780 s (~ 0.75 h). This shows that the time required to attain equilibrium (2–3 h) in these experiments is quite adequate for the saturation of the sample.

EFFECT OF CROSS-LINKING

Table III shows the hysteresis data for the heat-treated and untreated hair from Figure 5. From Table III, we obtain an H_R value of 1.44 (31.44/21.88) for heat-treated hair. This value is close to 1.45, based on actual area measurement. This shows that heat-treated hair is 44% better in retaining moisture compared with the untreated hair. Because hair fiber undergoes cross-linking at these temperatures, diffusion rate is considerably reduced, locking-in the moisture. Although the fiber is cross-linked, during sorption, the restraining effect on diffusion is less because of swelling. However, during desorption, because of cross-linking and fiber shrinkage, diffusion rate is drastically reduced, thus retaining the sorbed water. Quantitatively, cross-linking with heat treatment alone, or in combination with multifunctional low molecular weight compounds capable of penetrating the hair, has a better effect of locking-in moisture than rinse-off conditioning actives. This can be seen clearly by comparing the H_R values in Tables II and III.

Table III
Hysteresis Data of Heat-Treated (120°C for 1 h) and Untreated Hair

RH (%)	Untreated H_i	Heat-treated H_i
10	2.50	3.00
20	2.43	4.00
30	2.50	4.25
40	2.75	4.00
50	2.94	3.69
60	2.94	3.56
70	2.56	3.50
80	2.13	3.38
90	1.13	2.06
ΣH_i	21.88	31.44

PRODUCT EVALUATION

Determining H_R values for hair treated with a product with respect to the corresponding untreated hair can be useful in evaluating the moisturizing potential of the product. Although the earlier results with rinse-off conditioners were not favorable, it is possible to formulate products which show significant moisturizing capability. To demonstrate the possibility of using this approach, two different hair samples treated with two different products (compositions confidential) along with the corresponding control sample of hair were subjected to the DVS experiment as aforementioned at 25°C. Sorption-desorption isotherms of these samples are shown in Figures 7–9. Comparing the areas of the hysteresis loops, we can almost “see” the effects.

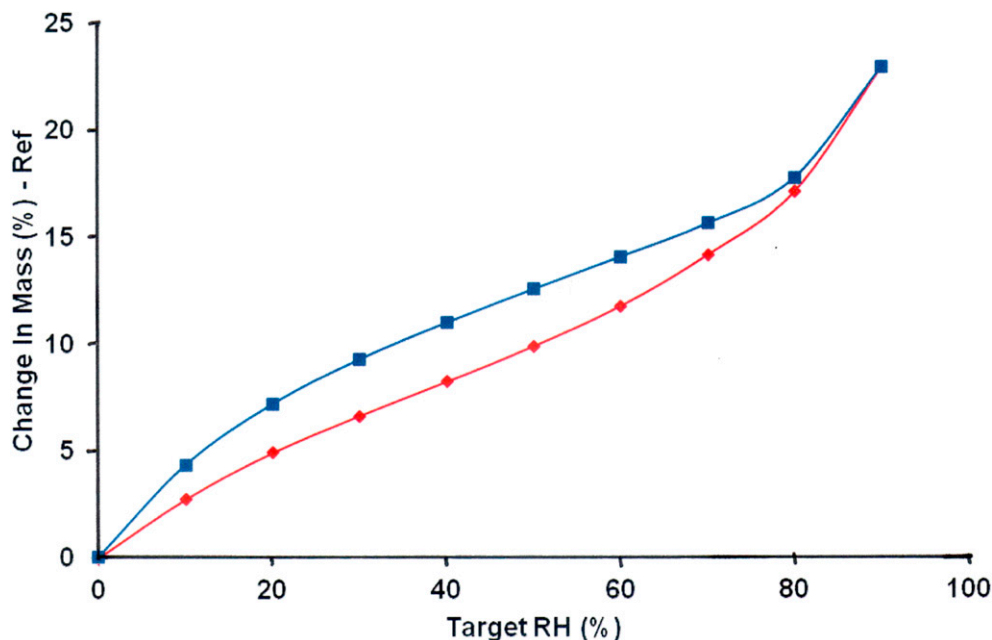


Figure 7. Sorption-desorption isotherms of hair with product 1.

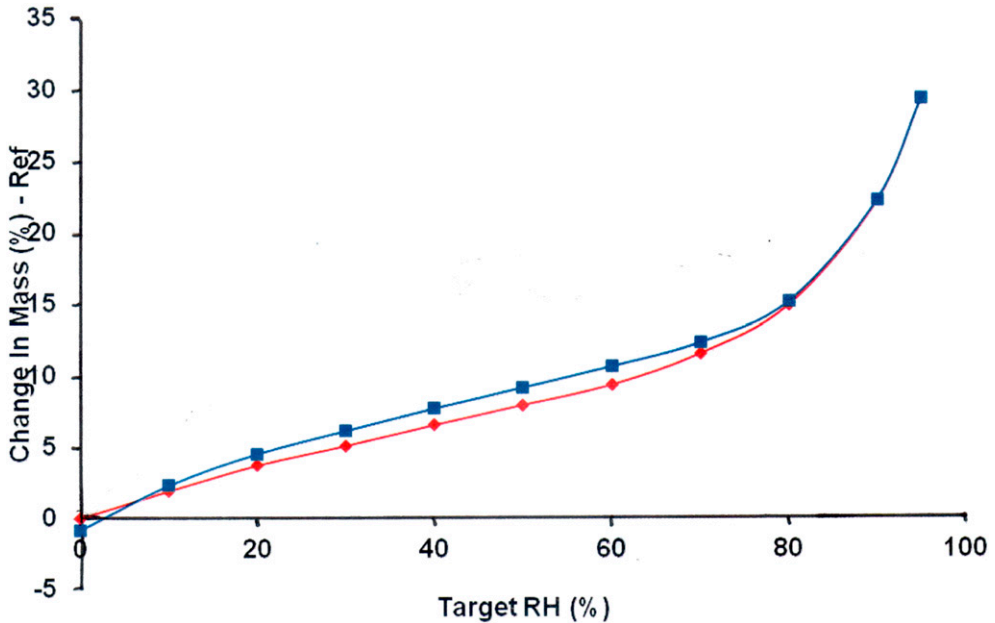


Figure 8. Sorption-desorption isotherms of hair treated with product 2.

Based on the areas of hysteresis loops, Figures 7–9 clearly show that product 1 retains more moisture than product 2 with reference to the control hair. This is clearly shown in the hysteresis plots of Figure 10.

Figure 10 shows that the data useful for product comparison lies in the 10–60% RH range. This is desirable because this is also the range of humidities over which cosmetic products perform the best. The area of the hysteresis loops from Figures 7–9 are shown in Table IV.

The data in Table IV show that product 1 is more like a conditioner capable of moisturizing hair. H_R value of 1.42 suggests that it is 42% better in retaining moisture than the untreated hair; on the other hand, product 2 ($H_R = 0.58$) is 42% worse in retaining water than the untreated hair and, therefore, may be useful as a styling (and style holding) and anti-frizz product.

To check the reliability of hysteresis measurement by this method, five measurements of hysteresis were made on an untreated sample of hair. Hysteresis data are shown in Table V.

The data in Table V show that both hysteresis values as a function of RH, as well as the areas of the hysteresis loops, have good reproducibility. Of course, it depends on the sample uniformity. Because of this, we could quantify the efficacy of cosmetic products and grooming processes in moisturizing hair with a limited number of experiments, using carefully prepared hair samples.

THE NATURE OF WATER SORPTION IN HAIR

Sorption of water in hair from vapor occurs by molecular diffusion. Molecules from the vapor condense on the surface to form an assemblage of water molecules, establishing a

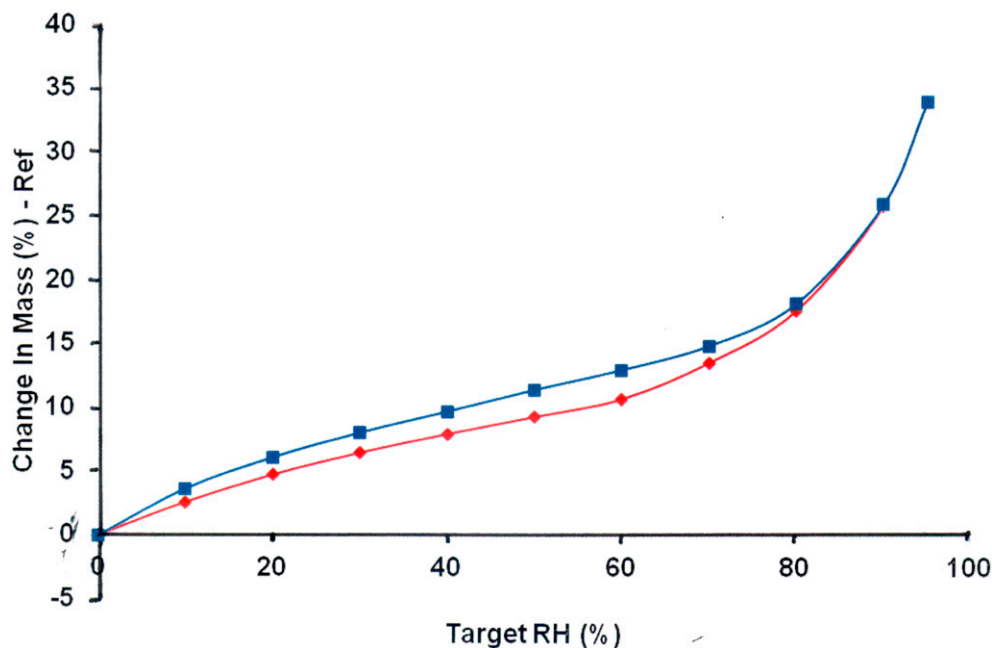


Figure 9. Sorption-desorption isotherms of untreated control hair.

concentration gradient necessary for diffusion into the hair. Because the cuticle cells are highly cross-linked with cystine, the diffusion does not occur through the cuticle cells. Instead, they diffuse through the CMC between the cuticle cells, then on to the CMCs between the cuticle and the cortex and then finally through the CMCs of the cortex into the cortical cells. Adsorption occurs on the inner surfaces of the pores in the entire fiber, rather than the geometrical surface of the fiber only (which is generally much smaller than the total surface area of the pores). The sorption isotherm reflects the nature of this adsorption. For example, the sorption of water into hair from the vapor is known to follow the BET isotherm (11). Molecules diffusing into the hair close to 0% RH form a monolayer which is tightly bound to the keratin by strong hydrogen bonds (5–8 kcal/mole). Subsequent adsorption occurs in multiple layers until about 60–70% RH. Following this, adsorption occurs by capillary condensation, leading to significant swelling of the fiber. The hydrogen bond strength decreases in subsequent layers following the first monolayer, until it approaches the strength of the hydrogen bond in water at that temperature.

The amount of water adsorbed per unit mass of hair depends on two characteristics of the substrate, e.g., the surface area of the pores and the total volume of the pores. Thielmann et al. (12) have determined the BET surface area of hair fibers by inverse gas chromatography (IGC) using hexane and water as the dispersive and polar probes, respectively. Their value is $0.3 \text{ m}^2/\text{g}$. Surface area of hair has also been determined by Hessefort et al. (13) by nitrogen adsorption and their value of $0.4 \text{ m}^2/\text{g}$ (total pore volume = $0.000689 \text{ cm}^3/\text{g}$) agrees reasonably well with that determined by the IGC method. The geometric cylindrical (assumed) surface area of hair based on a density of $1.38 \text{ g}/\text{cm}^3$ and $100 \text{ }\mu\text{m}$ in diameter is only $0.055 \text{ m}^2/\text{g}$. The surface area of the pores (BET surface area) is nearly seven times the geometric surface area of the assumed cylindrical hair fibers.

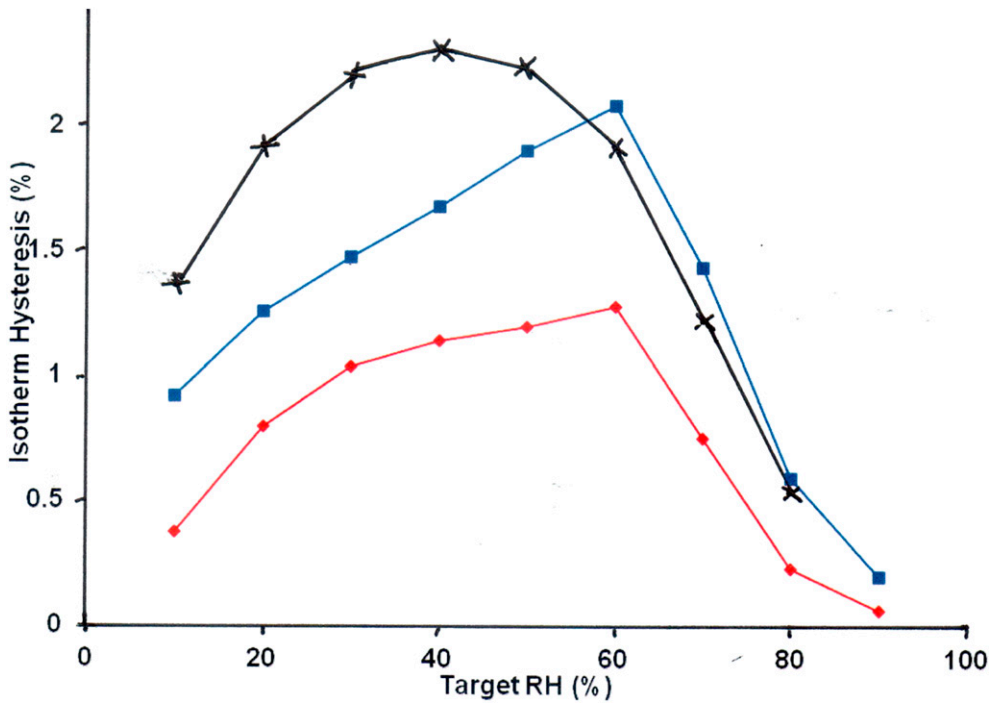


Figure 10. Hysteresis plots of hair treated with products 1 and 2 along with that of the control hair. Product 1 (x); product 2 (◇); untreated (□).

Using the surface area ($0.4 \text{ m}^2/\text{g}$) and the total pore volume ($0.000689 \text{ cm}^3/\text{g}$) of hair from reference 12, we can calculate the number of molecular layers adsorbed on the BET surface area. The average thickness t of the adsorbed water film is given by the following equation:

$$t = (0.000689 \times 10^{21}) / (0.4 \times 10^{18}) = 1.723 \text{ nm}.$$

The geometric thickness of a water molecule based on the density and the Avogadro's number is $\sim 0.33 \text{ nm}$. This leads to the number of adsorbed molecular layers to be about 5. This apparently looks reasonable, considering the surface energy of hair which is quite low (about $30\text{--}40 \text{ mJ}/\text{m}^2$) (14). However, the sorption isotherm tells a completely different story. For example, the amount of water sorbed in untreated hair is $\sim 4\%$ at 20% RH. Assuming the density of water as $1.0 \text{ g}/\text{cm}^3$, the volume of water sorbed is $0.04 \text{ cm}^3/\text{g}$. This is nearly 58 times the BET pore volume ($0.04/0.000689 = \sim 58$). This discrepancy suggests that a large part of water is not held in the nanoporous regions of hair, which are

Table IV
Hysteresis Loop Areas from Figures 7–9 in the 10–60% RH Range

Loop area 10–60% RH	Product 1	Untreated	Product 2
$\sum H_i (\%)$	14.23	10.0	5.84
H_R	1.42	1.0	0.58

Table V
Hysteresis Data for Untreated Hair Used in This Study

RH (%)	Hysteresis, H (%)					Average H	95% confidence level
	S1	S2	S3	S4	S5		
10	0.88	0.95	0.9	1.01	0.92	0.93	0.063
20	1.2	1.31	1.22	1.32	1.26	1.26	0.066
30	1.49	1.49	1.45	1.54	1.47	1.49	0.042
40	1.88	1.82	1.83	1.72	1.67	1.78	0.107
50	2.22	2.24	2.32	2.08	1.9	2.15	0.205
60	2.33	2.45	2.73	2.24	2.07	2.36	0.306
70	1.28	1.4	1.92	1.29	1.43	1.46	0.326
80	0.55	0.65	0.71	0.51	0.59	0.60	0.099
90	0.17	0.34	0.19	0.05	0.20	0.19	0.128
ΣH_i	12.00	12.65	13.27	11.76	11.51	12.24	0.894

accounted for by the BET surface area. The large pores which contribute very little to the BET surface area hold a much larger fraction of water. These could be the regions covered by the medulla, CMCs, and intermacrofibrillar materials (15), which are known to be less keratinous (more hydrophilic).

Rowen and Blaine (16) from the National Bureau of Standards have compared the BET pore surface areas determined by sorption of water and nitrogen on a series of materials. For wool, their data are 206 and 0.96 m²/g for water and nitrogen, respectively. Similar data for nylon are 45 and 0.31 m²/g, respectively. However, for titanium dioxide (TiO₂), the corresponding values are 7.0 and 7.9 m²/g, respectively. This clearly shows that the BET surface areas given by water sorption depend on the swellability of the substrate. Keratin fibers swell ~15%, whereas nylon swells only ~4% and TiO₂ does not swell.

Nonuniform distribution of water in keratin fibers has been known from earlier studies of Spei and Zahn (17). These authors observed that the swelling of the matrix between intermediate filaments by X-ray diffraction was only 5.5% compared with the diametral swelling of 16% of the entire fiber.

In further studies of the distribution of water in hair using D₂O and small angle neutron scattering (SANS), Murthy et al. (18) found that the amount of water sorbed into the amorphous matrix between intermediate filaments (nanoporous region) was relatively small compared with the total volume of water which was held in the fiber. These are assumed to be the smallest pores. The exact distribution in the larger pores in the fiber still remains unknown. The analysis of sorption data presented earlier seem to confirm the X-ray and the SANS results.

CONCLUSIONS

This work has shown that the strength of interaction of water with hair can be studied by sorption and desorption of water into hair by DVS as a function of relative humidity. S-D isotherms yield a hysteresis loop, the area of which is related to the intensity of water-hair interaction. Thermodynamic origin of this interaction leads to irreversibility of the sorption-desorption process. Increase in entropy is related to the formation of a

swollen hair–water composite. A method has been developed to convert simple hysteresis data into a hysteresis ratio H_R which can quantify the ability of hair treated with products and processes to retain (or repel) moisture as compared with the corresponding untreated hair. Work described in this communication shows that cross-linking with heat is more effective in retaining moisture as compared with rinse-off conditioning actives. The work described in this communication can be used to evaluate “moisturizing” or “anti-moisturizing” actives and products. Such information will be useful for formulators. The nature of sorption of water into the hair substrate has been considered from a molecular perspective. Swelling of the sorbent has a major effect on the measurement of pore volume and surface area by the BET method. This analysis clearly shows that a large fraction of water is held in larger pores and is not accounted for by the BET analysis. This creates a discrepancy between the results of BET analysis by gas (nitrogen or carbon dioxide) adsorption and the DVS results obtained with sorption of water. Using carefully prepared hair samples, we have been able to show the effectiveness of DVS method in quantifying efficacy of cosmetic formulations and processes with a limited number of experiments where the effects were robust. In the case of weak effects, adequate number of replicates will be necessary to establish statistically significant outcomes.

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