

The Sorption of Water by Nylons*

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I. INTRODUCTION

The sorption of water by hydrophilic polymers has been the subject of many investigations and a review by McLaren and Rowen.¹ The sorption at low relative humidities where many isotherms are concave downward has been described in terms of modifications of the Langmuir isotherm, such as the B.E.T.² and White and Eyring³ isotherms. All of these consider the sorption at localized sites. Katz⁴ has pointed out the similarity between polymers swollen with water and solutions of compounds such as sulfuric acid. Rowen and Simha⁵ have used the Flory-Huggins equation to describe the sorption of water at high relative humidities where the isotherms are concave upward.

Pauling⁶ has suggested that in the samples of nylon examined by Bull⁷ the number of localized sites corresponded to 6% of the amide groups, the remainder being bonded to other amide groups. In the present work, samples of nylons in the form of unoriented films were annealed to give a relatively high constant level of crystallinity. The sorption isotherms at 23°C. for these samples were concave upward over the entire range of humidity, suggesting that there were essentially no unbonded amide groups. Somewhat similar sorption isotherms were observed by Kargin for glasses of glucose, caprolactam dimer, and other compounds of low molecular weight.⁸

II. SORPTION ISOTHERMS

The sorption isotherms of films of nylon 66 (polyhexamethylene adipamide) and nylon 610 (polyhexamethylene sebacamide) at 23°C. are shown in Figure 1. The sample of nylon 66 was an extruded film 0.010 in. thick annealed at 250°C. for 10 min. It was 57% crystalline based on a density scale which had been calibrated by infrared techniques.⁹

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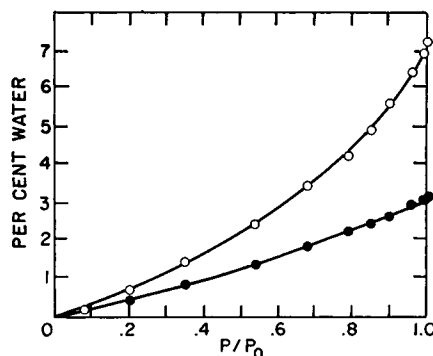


Fig. 1. Sorption isotherms for water in nylon resins at 23°C. Points, experimental; lines, calculated from Flory-Huggins equation. (O) Nylon 66, 57% crystalline, $\chi_1 = 1.46$; (●) nylon 610, 47% crystalline, $\chi_1 = 2.18$.

The film of nylon 610 was compression molded, quenched in ice water, and annealed at 200°C. for 10 min. It was 47% crystalline.

It has been reported¹⁰ that the amount of water absorbed at a given temperature and relative humidity is proportional to the amorphous fraction. Therefore, the Flory-Huggins¹¹ treatment of polymer solutions has been applied to a mixture consisting of the absorbed water and the amorphous portions of the nylon. Following the conclusions of Rowen and Simha,⁵ the contribution of the mechanical force opposing swelling to the total free energy change has been neglected.

The free energy of mixing is given by the following expression:

$$\Delta F_M = kT [n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 n_1 v_2] \quad (1)$$

where n_1 and n_2 are the number of molecules of water and polymer, respectively, v_1 and v_2 are the volume fractions of water and polymer, and χ_1 is the interaction energy per molecule of water at infinite dilution divided by kT . Differentiation of ΔF_M with respect to n_1 leads to the following equation for the sorption isotherm when the molecular weight of the polymer is high.

$$\ln (P/P_0) = \frac{1}{kT} \left(\frac{\partial \Delta F_M}{\partial n_1} \right) = \ln v_1 + v_2 + \chi_1 v_2^2 \quad (2)$$

P and P_0 are the partial pressures of water vapor over the polymer and liquid water, respectively. Equation (2) is commonly known as the Flory-Huggins equation.

The values of χ_1 calculated from each point on the experimental isotherms are given in Table I. This parameter is nearly constant between 35 and 100% relative humidity. An amorphous transition occurs in nylon at 35% R.H. and 23°C. Below this transition, the amount of water absorbed is very

TABLE I
Sorption Isotherms for Nylon Resins at 23°C.

P/P_0	% Water, Dry basis	v_1	χ_1
Nylon 66, density = 1.1504 g./cc., 57% crystalline			
0.08	0.16	0.0040	2.02
0.20	0.66	0.0161	1.59
0.35	1.4	0.0336	1.48
0.54	2.4	0.0563	1.48
0.68	3.4	0.0780	1.46
0.79	4.2	0.0946	1.48
0.85	4.9	0.1086	1.47
0.90	5.6	0.1223	1.45
0.96	6.4	0.1373	1.45
0.99	6.9	0.1465	1.45
1.00	7.2	0.1519	1.44
Nylon 610, density = 1.0935 g./cc., 47% crystalline			
0.20	0.4	0.0078	2.29
0.35	0.8	0.0155	2.20
0.54	1.3	0.0249	2.21
0.68	1.8	0.0342	2.17
0.79	2.2	0.0414	2.16
0.85	2.4	0.0450	2.18
0.90	2.6	0.0486	2.18
0.96	2.9	0.0539	2.16
0.99	3.0	0.0556	2.17
1.00	3.1	0.0574	2.16

TABLE II
Values of the Interaction Parameter χ_1 for Several Polymers Saturated with Water

Polymer	Temp., °C.	χ_1	Ref.
Collagen	28	0.77	5
Serum albumen	25	0.87	5
Viscose	25	1.00	5
Wool	25	1.06	5
Silk	25	1.15	5
Cellulose	25	1.25	5
Nylon 66	23	1.44	this work
Polyvinyl acetate	40	2.0	12
Nylon 610	23	2.16	this work

small and it is difficult to determine χ_1 accurately. In Figure 1, the sorption isotherms calculated from eq. (2) using constant values of χ_1 are compared with the experimental points.

The amount of water absorbed at saturation is inversely related to χ_1 and directly related to the concentration of polar groups in the polymer. The values of χ_1 for several hydrophilic polymers are given in Table II.

III. ACTIVITY OF NYLON POLYMER UNITS

The activity of the polymer units relative to pure polymer, a_u , is obtained as follows:

$$\begin{aligned} \ln a_u &= \frac{1}{kT(\text{D.P.})} \left(\frac{\partial \Delta F_M}{\partial n_2} \right) \\ &= - \left(\frac{V_u}{V_1} \right) [v_1 - \chi_1 v_1^2] \end{aligned} \quad (3)$$

where (D.P.) is the number of polymer units per molecule, and V_1 and V_u are the molar volumes of water and the polymer units, respectively. For this purpose, a polymer unit is defined to include one amide group.

When v_2 is close to unity, $v_1 = n_1 V_1 / n_u V_u$, where n_u is the number of polymer units in the amorphous regions. Then eq. (3) becomes:

$$\begin{aligned} -\ln a_u &= \frac{V_u}{V_1} \cdot \frac{n_1 V_1}{n_u V_u} (1 - \chi_1 v_1) \\ &\cong n_1 / n_u \cong -\ln \left(\frac{n_u}{n_1 + n_u} \right) \end{aligned} \quad (4)$$

so that

$$a_u \cong n_u / (n_1 + n_u) \quad (5)$$

It is seen from Table III that eq. (5) is accurate at much higher water contents than would have been expected on the basis of these approximations.

It follows from the Duhem-Margules equation

$$d \ln a_1 / d \ln x_1 = d \ln a_2 / d \ln x_2 \quad (6)$$

and from eq. (5) that

$$P/P_0 = K [n_1 / (n_1 + n_u)] \quad (7)$$

It turns out that eqs. (2) and (7) both fit the experimental data very well. Equation (7), which is a modified form of Henry's law, does not appear to have an adequate theoretical basis. Therefore, eq. (2) which was derived from a lattice model for polymer solutions is preferred.

TABLE III
Activity of Polymer Units

P/P_0	a_u [from eq. (3)]	$n_u/(n_1 + n_u)$
Nylon 66		
0.08	0.998	0.978
0.20	0.913	0.912
0.35	0.830	0.830
0.54	0.741	0.741
0.68	0.669	0.668
0.79	0.623	0.620
0.85	0.588	0.583
0.90	0.557	0.550
0.96	0.527	0.517
0.99	0.511	0.498
1.00	0.501	0.488
Nylon 610		
0.20	0.944	0.944
0.35	0.894	0.894
0.54	0.839	0.839
0.68	0.789	0.790
0.79	0.755	0.755
0.85	0.739	0.738
0.90	0.723	0.723
0.96	0.701	0.700
0.99	0.694	0.693
1.00	0.687	0.686

TABLE IV
Changes in the Volume of Nylons on the Sorption of Water

P/P_0	% Water, dry basis	Density, g./cc.	Volume, cc./g. of dry polymer
Nylon 66			
0	0	1.1504	0.8693
0.08	0.16	1.1511	0.8701
0.20	0.66	1.1528	0.8731
0.35	1.4	1.1560	0.8772
0.54	2.4	1.1573	0.8848
0.68	3.4	1.1564	0.8941
0.79	4.2	1.1578	0.9000
0.85	4.9	1.1568	0.9068
0.90	5.6	1.1576	0.9122
0.96	6.4	1.1568	0.9198
0.99	6.9	1.1538	0.9265
1.00	7.2	1.1535	0.9293
Nylon 610			
0	0	1.0935	0.9145
0.20	0.4	1.0955	0.9165
0.35	0.8	1.0957	0.9200
0.54	1.3	1.0990	0.9217
0.68	7.8	1.0986	0.9266
0.79	2.2	1.0988	0.9301
0.85	2.4	1.0985	0.9322
0.90	2.6	1.0985	0.9340
0.96	2.9	1.0988	0.9365
0.99	3.0	1.0986	0.9315
1.00	3.1	1.0985	0.9386

IV. VOLUME EFFECTS

Nylon is more dense than water. Nevertheless, as nylon absorbs water, its density increases. The volume of the mixture is less than the sum of the volumes of the components. These effects are described in Table IV. The partial specific volume of water in nylon, $\partial V/\partial W$ appears to be a linear function of P/P_0 varying from 0.46 cc./g at 0% R.H. toward 1.0 cc./g. at 100% R.H. for both nylons 66 and 610. In Figure 2, the experimental data for nylon 66 are compared with a curve representing an integral equation based on this assumption. Actually, the partial specific volume for water rises to 1.07 cc./g. at 95% R.H. and 1.19 cc./g. at 98% R.H. in nylon 66.

Similar, low values for the partial specific volume of water at low relative humidities have been reported for cellulose^{4,13} and sulfuric acid. In all these cases, the limiting value at 0% R.H. was close to 0.5 cc./g. However, when water is absorbed by polyvinyl acetate¹² or polymethyl methacrylate,¹⁴ essentially exact volume additivity has been observed. This suggests that when a change in volume does occur, it is not because of the way in which a water molecule bonds to a substrate, but rather because of the type of bond which the water displaces. In nylon, cellulose, and sulfuric acid, there are intermolecular hydrogen bonds which obey rather strict steric requirements. These bonds prevent the other portions of the molecules from packing as closely as they otherwise would, and when one of them is broken by a water molecule, there is a decrease in total volume. In polyvinyl acetate and polymethyl methacrylate which do not have hydrogen bonds, no change in volume accompanies the sorption of water.

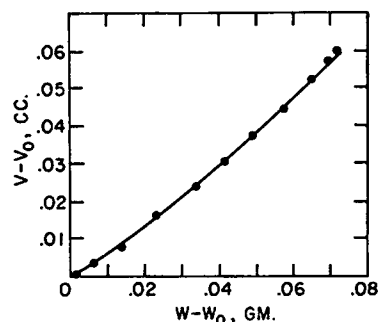


Fig. 2. Changes in volume and weight of 1 g. of nylon 66 during the sorption of water. (●) Experimental; (—) calculated assuming that the partial specific volume of water increases linearly with relative humidity from 0.46 cc./g. at 0% R.H. to 1.0 cc./g. at 100% R.H.

V. HEAT OF SORPTION

In the Flory-Huggins treatment of polymer solutions, the first two terms on the right-hand sides of eqs. (1) and (2) represent entropy contributions and the final terms are heat terms. Thus, the partial heat of sorption per mole of water is

$$\Delta\bar{H}_1 = RT\chi_1v_2^2 \quad (8)$$

In practice, the Flory-Huggins equation has given considerably better agreement with experiment than the separated entropy and heat terms. One possible refinement is to consider the effect of changes in volume. Katz⁴ has pointed out that while there is no exact proportionality between the decrease in total volume and the heat of sorption for water in hydrophilic sorbents, the ratio between them is always of the same order of magnitude. One of the assumptions which was made in the derivation of the Flory-Huggins equation was that there was no change in volume on mixing.

The effect of changes in volume has been treated by Scatchard¹⁵ and Hildebrand.¹⁶

Except for higher-order effects, changes in volume do not affect changes in free energy.

$$(\Delta\bar{F}_1)_P = (\Delta\bar{A}_1)_V \quad (9)$$

The partial molar heat of sorption under constant pressure is

$$(\Delta\bar{H}_1)_P = (\Delta\bar{E}_1)_V + T(\partial P/\partial T)_V \Delta\bar{V}_1 \quad (10)$$

$$= RT\chi_1v_2^2 + T(\alpha/\beta) \Delta\bar{V}_1 \quad (11)$$

where $\alpha = (1/V)(\partial V/\partial T)_P$, the coefficient of thermal expansion, $\beta = -(1/V)(\partial V/\partial P)_T$, the compressibility, and $\Delta\bar{V}_1$ is the partial molar change of volume of the total system of polymer plus water. The coefficients of thermal expansion were estimated from data on linear expansion. Values for the compressibility were taken from the work of Bridgman.¹⁷ His value for nylon 66 was used up to 35% R.H. This is in good agreement with the values of Weir¹⁸ on dry wool and silk fibroin. At higher humidities values based on our experience with other polymers were used. These values are given in Table V.

TABLE V
Coefficients of Thermal Expansion and Compressibility for Nylon 66 at 23°C.

	α , deg. ⁻¹	β , atm. ⁻¹	$T \alpha/\beta$, atm.
Up to 35% R.H.	2.28×10^{-4}	1.37×10^{-5}	4.93×10^3
Above 40% R.H.	3.15×10^{-4}	2.26×10^{-5}	4.12×10^3

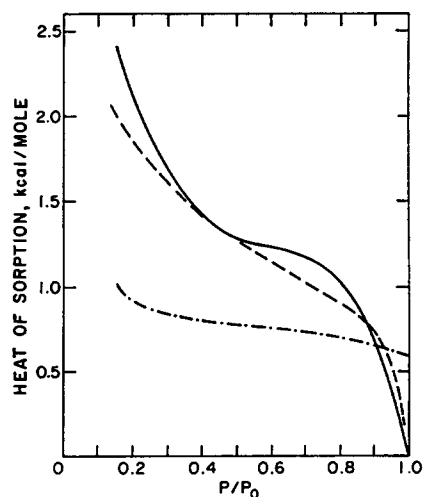


Fig. 3. Heat of sorption of water in nylon 66. (---) $(\Delta\bar{E}_1)_V = RT\chi_1v_2^2$; (-·-) $(\Delta\bar{H}_1)_P = RT\chi_1v_2^2 + T(\alpha/\beta)\Delta\bar{V}_1$; (—) $(\Delta\bar{H}_1)_P$ = experimental results of Speakman and Saville.

In Figure 3, the heats of sorption for water in nylon 66 at constant volume [eq. (8)] and at constant pressure [eq. (11)] are compared with experimental values calculated from measurements by Speakman and Saville¹⁹ of the dependence of the sorption isotherms of undrawn fibers of nylon 66 on temperature. The agreement between the experimental and calculated values under constant pressure is quite good.

Above 90% R.H., the volume of the polymer increases more than the volume of the additional water. This expansion is just enough to alter the Flory-Huggins equation at constant pressure to satisfy the condition

$$\Delta\bar{F}_1 = \Delta\bar{H}_1 = \Delta\bar{S}_1 = 0$$

when $P = P_0$.

VI. CONCLUSIONS

Comparison with earlier work^{1,6,7} shows that the sorption isotherms for water in nylon 66 and nylon 610 are simplified as a result of annealing. This treatment presumably results in improved bonding between amide groups in the amorphous portions, and thus greatly reduces the tendency to absorb water at low humidities. The Flory-Huggins equation is much more successful in describing the sorption isotherms over the entire range of humidity than in many systems where strong interactions between solvent molecules and specific sites on the polymer are less probable. This may be due partly to the fact that the volume fraction of nylon

is always quite large and the polymer segments must be arranged approximately at random in space.²⁰ The separated heat and entropy terms of the Flory-Huggins equation are also in unusually good agreement with experiment provided changes in volume are considered. While the mechanism of these changes in volume is not entirely understood, they are believed to reflect the breaking of intermolecular hydrogen bonds which tend to keep neighboring segments "at arm's length" and prevent the hydrocarbon portions of the molecules from packing as well as they otherwise would.

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Synopsis

The sorption isotherms of annealed films of nylons 66 and 610 at 23°C. are well described by the Flory-Huggins equation at all humidities. The partial specific volume of water varies from 0.46 cc./g. at 0% R.H. to more than 1.0 cc./g. at 100% R.H. The experimental partial molar heats of sorption are in good agreement with values calculated from the theory, provided allowance is made for the changes in volume on mixing.

Résumé

Les isothermes de sorption des films recuits de nylon 6-6 et de nylon 6-10 à 23° sont bien décrits par l'équation de Flory-Huggins à tous les degrés d'humidité. Le volume spécifique partiel de l'eau varie de 0,46 ml/g à 0% d'humidité relative, jusqu'à plus de 1,0 ml/g à 100% d'humidité relative. On obtient une bonne concordance entre les valeurs expérimentales des chaleurs molaires partielles de sorption et les valeurs calculées d'après la théorie à condition de faire certaines réserves quant aux changements du volume lors du mélange.

Zusammenfassung

Die Sorptionsisothermen getemperter Filme aus Nylon 66 und 610 bei 23°C können durch die Gleichung von Flory und Huggins bei allen Feuchtigkeitsgraden gut wiedergegeben werden. Das partielle spezifische Volumen des Wassers ändert sich von 0,46 ml/g bei 0% relativer Feuchtigkeit zu mehr als 1,0 ml/g bei 100% relativer Feuchtigkeit. Die experimentellen Werte für die partiellen molaren Sorptionswärmern stimmen mit den aus der Theorie berechneten Werten gut überein, vorausgesetzt, dass die Volumsänderung beim Mischen berücksichtigt wird.

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