Water Vapor Sorption by Amylose and Cellulose Acetates

H. M. BARNES,* C. SKAAR, and P. LUNER, *State University of New York College of Environmental Science and Forestry, Syracuse, New York 13210*

Synopsis

Experimental sorption isotherms for amylose acetate (ADA) and cellulose acetate (CDA) are discussed in terms of the B.E.T. theory and the Hailwood–Horrobin theory. The B.E.T. theory predicted a good fit to most of the experimental isotherms up to 0.8 relative vapor pressure. A somewhat better fit was found with the solution theory of Hailwood–Horrobin over the entire range of relative vapor pressures. Annealing had little effect on the sorption properties of CDA, but significantly reduced sorption in ADA. This was attributed to a higher degree of ordering in the amylose polymer.

INTRODUCTION

Sorption behavior of polymers has been described by several theoretical models.[1,2,3] Two of these models, the B.E.T. multilayer and Hailwood–Horrobin solution sorption theories, were used to evaluate water vapor sorption by cellulose acetate and amylose acetate.

The B.E.T. theory is an extension of the surface sorption theory proposed by Langmuir.[4] By means of statistical thermodynamics, Brunauer, Emmett, and Teller[5] were able to extend Langmuir's theory to include sorption of the absorbate in multilayers. Two assumptions are made in the B.E.T. equation: (1) the heat of condensation of free water equals the binding energy for layers other than the first, and (2) the evaporation–condensation mechanism is the same for all layers other than the first. The form of the isotherm is represented by the B.E.T. equation:

$$\frac{h}{m(1-h)} = \frac{1}{m_m C} + \frac{(C-1)h}{m_m C} \tag{1}$$

where h = relative vapor pressure of water, m = fractional moisture content of the polymer, m_m = moisture content of the monolayer, and C = a constant. This theory has been found to adequately describe[2] the sorption of water vapor in cellulosic polymers below 0.5 relative vapor pressure (rvp). Attempts to account for the sorption at relative vapor pressures greater than 0.5 have met with varying degrees of success.[5-11]

* Present address: Forest Products Utilization Laboratory, Mississippi State University, State College, Mississippi 39762.
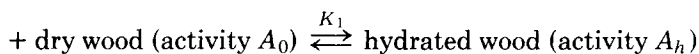
In general, the solution sorption theories assume that the polymer is composed of ordered and unordered regions with sorption occurring by hydration of the primary sites in the amorphous region followed by their dissolution in the surrounding water. These theories have been found to be useful in the relative vapor pressure regions above 0.5. Barrie[12] has discussed several of these models in detail.

One of the solution models has been used extensively for textile materials. This theory, derived by Hailwood and Horrobin,[13] considers sorbed water to exist as an ideal solution of three species—polymer, hydrated polymer, and dissolved water. Application of this model produces a measure of water of hydration, condensed water, and the accessibility of sites for sorption. An analysis of the model leads to the equation
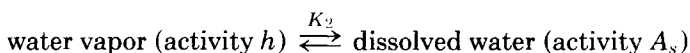
$$\frac{mW}{18} = \frac{K_2 h}{1 - K_2 h} + \frac{K_1 K_2 h}{1 + K_1 K_2 h} \tag{2}$$

where m = fractional moisture content, W = molecular weight of polymer per mole of hydrated water, h = relative vapor pressure, K_1 = equilibrium constant between the three species, and K_2 = equilibrium constant between the dissolved water and its relative vapor pressure. These equilibrium constants have been given by Skaar[14] as follows:

dissolved water (activity A_s)

$$+ \text{ dry wood (activity } A_0) \overset{K_1}{\rightleftarrows} \text{ hydrated wood (activity } A_h)$$

and

$$\text{water vapor (activity } h) \overset{K_2}{\rightleftarrows} \text{ dissolved water (activity } A_s)$$

This research describes the sorption of water vapor by amylose and cellulose acetates as affected by heat treatment, the degree of acetylation, and the solid-state organization of the polymers through use of the B.E.T. and Hailwood–Horrobin theories. This work was undertaken as a part of a comprehensive research effort to characterize film-forming materials for potential use in reverse osmosis. Amylose acetate represents a material on which little information is available.

EXPERIMENTAL

Preparation of Materials

Three dense films were prepared for this study—cellulose diacetate and amylose diacetate (designated CDA and ADA, respectively) and cellulose triacetate (designated CTA). The CDA films were prepared from a commercial cellulose acetate powder (39.8% acetyl), E-398-3, supplied by Eastman Chemical Products, Inc. The triacetate powder was obtained from the same source.

The casting dope was prepared by dissolving the powder in reagent-grade acetone to yield a 30% solution of the acetate, which was subsequently diluted, filtered, and reconcentrated to 30%. Casting was done at ambient conditions (23°C, 50% relative humidity) by automatically passing a polished glass plate

under a doctor blade preset to a given wet-film thickness. The films were allowed to dry in place at room temperature until no odor of acetone could be detected. The films were then immersed in distilled water and floated off the glass plates and stored until used.

The amylose used in this study was a high-purity white powder supplied by the National Starch Company. The acetylation procedure was that described by Jeanes and Jones.[15] It was a formamide activation technique, followed by acetylation to the triacetate with acetic anhydride and precipitation in ice water. Following an acid hydrolysis to the diacetate, the casting dope was prepared in an identical manner to that of cellulose acetate. A degree of acetylation of 41.2% was determined using ASTM Standard D871-63.[16]

Both diacetate films were heated (designated HT) in order to ascertain the effect of heat treatment on the sorptive properties. To accomplish this, the untreated ADA films were placed in aluminum restraining rings measuring 57.1 mm O.D. by 32.5 mm I.D. which were clamped with machine screws. The assembled rings were stacked in a stainless steel cup containing distilled water, and the cup was placed on a rack in a pressure cooker partially filled with water. The samples were then annealed for 30 min at 15 psig. The temperature inside the cooker was approximately 120°C. After cooling, the films were removed and stored in distilled water. The CDA films were heated unrestrained for 4 min at 70°C in water to simulate more closely the annealing of membranes.

One commercially available asymmetric "Loeb-type" cellulose acetate (39.8% acetyl) membrane was investigated. Designated RO-97, it was supplied in a 25-square-foot roll by Eastman Chemical Products, Inc. Prior to its use, samples of the membrane were washed to remove any additives.

Determination of Sorption Isotherms

Sorption isotherms for the various materials were determined using a Cahn Model RG recording balance in a vacuum system. After calibration of the system, a sample measuring approximately 2 cm $\times$ 5 cm was threaded on a nichrome wire and attached to the weighing mechanism. The entire system was evacuated to 0.4 μm Hg or better as read on a McLeod gauge. Vapor from previously degassed liquid water was admitted to the weighing chamber, and the equilibrium weight and pressure were recorded. Vapor pressure was read on a Zimmerli gauge. The entire system was located in a temperature-humidity-controlled room. The sample and vapor source temperatures were controlled with a water bath to within 25° ± 0.1°C.

Subsequent desorption measurements were made by removing a given amount of vapor by vacuum and recording the equilibrium weight and pressure.

RESULTS AND DISCUSSION

The B.E.T. Theory

Equation (1) may be modified to include a restriction on the maximum number of layers which may form.[6] The equation is then written as

$$\frac{h}{m(1-h)} = \frac{1}{m_m C} \frac{1 + (C-1)(h) - C(h)^{n+1}}{1 - (n+1)h^n + nh^{n+1}} \tag{3}$$

TABLE I
Calculated Values from the B.E.T. Theory for Various Polymers and Thicknesses

Polymer	Thickness, μm	C	M_m,[b] %	Σ, (meter)^2/g	n	$E_l - E_L$, cal/g
CDA-UT	9.1	2.74	3.04	150	10	33.3
CDA-UTD[a]	9.1	10.64	4.04	200	8	77.8
CDA-UT	51.7	3.87	2.35	116	12	44.6
CDA-HT[c]	9.9	3.71	3.01	149	8	43.2
CTA	11.2	3.22	2.37	117	7	38.5
RO-97		5.18	2.58	127	11	54.2
RO-97D[a]		4.10	3.73	184	9	46.5
ADA-UT		3.07	1.73	85	12	37.0
ADA-HT[d]		3.02	1.65	81	9	36.4

[a] D = Desorption; all other values are for adsorption.
[b] $M_m = 100\ m_m$.
[c] Heat treated at 70°C for 4 min.
[d] Heat treated at 120°C for 30 min.

where n is the maximum number of water layers on any sorption site. Equation (3) reduces to eq. (1) when $n = \infty$ and to the Langmuir equation when $n = 1$.

Equation (1) was plotted as $h/[m(1 - h)]$ versus h for each experimental isotherm. These plots deviated from a straight line at relative vapor pressures greater than 0.5. Therefore, the equation of the line in the region from 0.0 to 0.5 rvp was used to obtain the B.E.T. constants C and m_m. The value of n producing a theoretical isotherm which best fit the experimental data was determined using eq. (3). These values are given in Table I.

The B.E.T. theory has been applied extensively to cellulosic polymers and good agreement between experimental isotherms, and the theory has been found[6] up to relative humidities as high as 70%. Limited data are available on cellulose acetate, and none exist for amylose acetate. As shown in Figure 1, the B.E.T. equation provides a good fit to the present data from a minimum rvp of 0.6 to a maximum of 0.8 rvp.

The B.E.T. constant C is defined by Stamm (2) as

$$C = K \exp \{- (E_l - E_L)/RT\} \qquad (4)$$

where K = a constant approaching unity, E_l = heat of adsorption, E_L = heat of condensation, R = gas constant, and T = absolute temperature. The quantity $(E_l - E_L)$ was calculated from eq. (4) by using the value for C in eq. (1) and assuming a K value of unity. These values, given in Table I, are in the same order of magnitude reported by Stamm for cellulosic materials,[2] indicating that the initial water bonding mechanism is similar.

One may calculate the effective contact area Σ, in (meters)^2/g, between water and polymer in solid solution using the expression given by Stamm[2] as

$$\Sigma = (aNm_m/M) \times 10^{-4} \qquad (5)$$

where a = area occupied by adsorbate molecule (taken as 14.8×10^{-16} cm^2 for water), N = Avogadro's number, and M = molecular weight of water. Referring to Table I, one notes that the accessible surface area and monomolecularly ad-
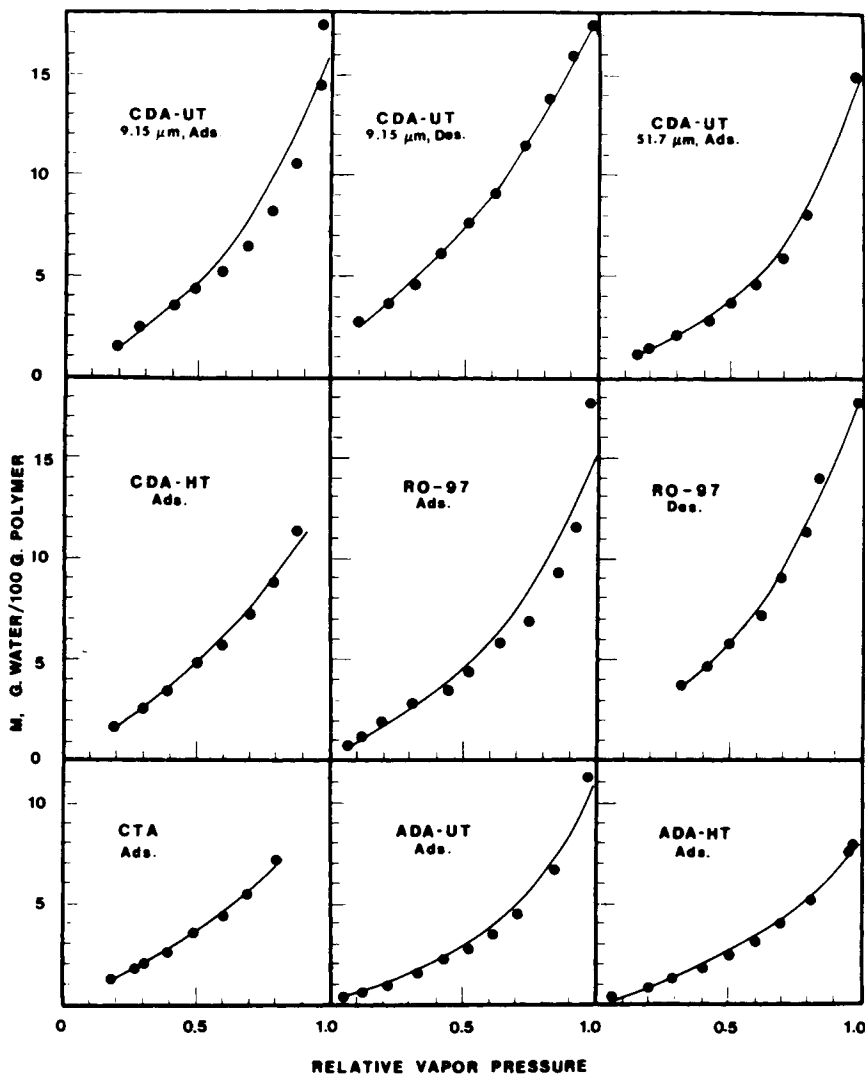
Fig. 1. Sorption isotherms predicted by the B.E.T. theory.

sorbed water are greater in desorption than in adsorption. Presumably, this is because during desorption more sorption sites are available than during adsorption.

The average accessible surface area of the 39.8% acetyl cellulose acetate in adsorption is 138 (meters)^2/g, compared with 83 (meters)^2/g for the amylose polymer with an acetyl content of 41.2%. This difference is most likely due to the higher crystallinity of the amylose acetate polymer.

Solution Theory of Hailwood–Horrobin

Equation (2) was algebraically transformed to the parabolic relationship

$$h/m = A + Bh + Ch^2$$

TABLE II
Physical and Derived Constants from the Hailwood–Horrobin Theory

Polymer	Thickness, μm	K_1	K_2	W, g/mole	$M_h{}^b$, %	$M_s{}^b$, %	$1800/W$, %
CDA-UT	9.1	1.506	0.773	428	2.3	14.4	4.2
CDA-UTD[a]	9.1	5.547	0.700	289	5.0	14.6	6.2
CDA-UT	51.7	2.110	0.812	557	2.0	14.0	3.2
CTA	11.2	1.380	0.722	460	2.0	10.2	3.9
CDA-HT[c]	9.9	2.305	0.774	435	2.6	14.2	4.1
RO-97		3.758	0.810	554	2.4	13.9	3.2
RO-97D[a]		1.499	0.699	271	3.4	15.4	6.6
ADA-UT		1.620	0.822	762	1.3	10.9	2.4
ADA-HT[d]		1.444	0.730	682	1.4	7.2	2.6

[a] D = Desorption; all other values are for adsorption.
[b] Predicted values at $h = 1.0$; $M_h = 100\ m_h$; $M_s = 100\ m_s$.
[c] Heat treated at 70°C for 4 min.
[d] Heat treated at 120°C for 30 min.

where h is the relative vapor pressure and m is the fractional moisture content; the constants A, B, and C are related to the fundamental constants K_1, K_2, and W as follows:

$$A = (W/18)\{1/K_2[K_1 + 1]\} \tag{7a}$$

$$B = (W/18)[(K_1 - 1)/(K_1 + 1)] \tag{7b}$$

$$C = (W/18)[K_1K_2/(K_1 + 1)] \tag{7c}$$

Equation (6) was fitted empirically using isotherm data and the constants were evaluated. Table II shows the derived values of the rate constants K_1 and K_2 and the grams of dry polymer per mole of sorption sites, W.

The total moisture content m can be separated into the water of hydration m_h and the water of solution m_s by the relationships

$$m_h = (18/W)[K_1K_2h/(1 + K_1K_2h)] \tag{8}$$

and

$$m_s = (18/W)[K_2h/(1 - K_2h)] \tag{9}$$

The value of $18/W$ is equivalent to that fractional moisture content at which the polymer is fully hydrated. It is higher than the value of water of hydration m_h at unity rvp, as is clear from Table II.

Isotherm plots of the water of solution M_s and water of hydration M_h, along with the total moisture content M_t predicted by the theory, are shown in Figure 2 for the various materials in the study. The experimental points are included for comparison.

Table II provides some interesting comparisons. For the two cases where desorption data are available, the value of W is lower for the desorption curve. This indicates that the moisture content of the fully hydrated polymer, calculated as
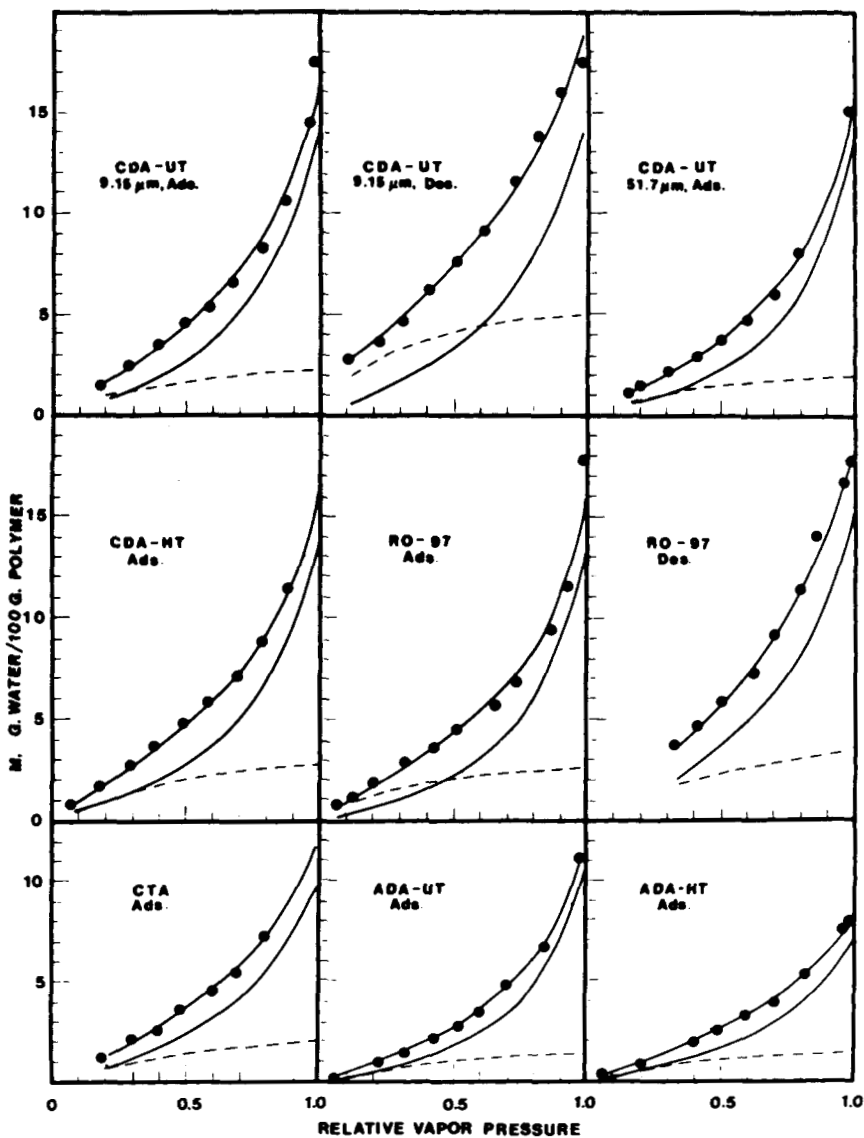
$$m = 18/W \tag{10}$$

Fig. 2. Sorption isotherms from the Hailwood–Horrobin theory showing the predicted values for water of hydration M_h (- - - -), water of solution M_s (——), and total water sorbed M (—●—).

is greater in desorption than in adsorption. This may be interpreted to mean that fewer sorption sites are available during adsorption than during desorption, as has been found in studies with wood.[6,17] When the polymer dries, some of the sorption or hydration sites crosslink, presumably through hydrogen bonding, and are unavailable for sorption.

As shown by eqs. (8) and (9) and Figure 2, the moisture present in the polymer can be separated into the water of hydration and water of solution. The curve for the former is of the Langmuir[4] form. The latter is characterized by sorption in several layers in which the attractive forces between the polymer and water and between water and water are about the same.
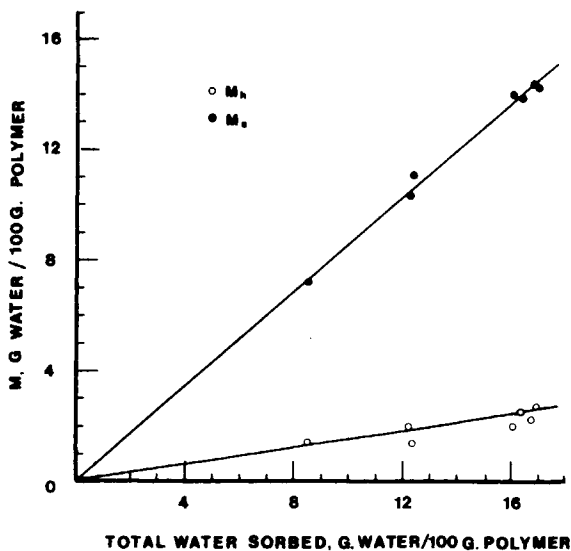
Fig. 3. Relationship between the total water sorbed at unit activity and manner in which it is held in polymer structure.

Figure 3 shows plots of the water of hydration M_h and the water of solution M_s (see Table II) as functions of the total moisture content M_t (equal to $M_s + M_h$) for each of the films and membranes tested at unity rvp. Both sets of points appear to show linear relationships going through the origin. This indicates that the ratio M_s/M_h in adsorption is approximately constant at unity activity, with a mean value of 6.1 for all the polymers. This may indicate that there are on the average 6.1 molecules of dissolved water per molecule of hydrated water for all of the polymers at unity water vapor activity.

Figure 4 compares the experimental isotherm points (M) with those predicted from the Hailwood and Horrobin equations $(M_h + M_s)$ in terms of the ratio $M/(M_h + M_s)$. For a perfect fit, this ratio should be unity. Most of the ratios vary from 0.95 to 1.05 over the rvp range.

Four of the polymers listed in Table II are identical with respect to polymer type: CDA-UT (two thicknesses), CDA-HT, and RO-97. There appears to be little difference attributable to thickness between the two CDA-UT films in terms of the monomolecular water content value M_h. The M_h adsorption values for the membrane, RO-97, and for the heat-treated material also fall in the range 2.0–2.5%. The total water sorbed for each of the four polymers is also similar. The M_h desorption values are higher than the corresponding values for adsorption. This is due to the greater availability of sorption sites during desorption.

Table II shows that there is no essential difference between the CDA film and the membrane RO-97 under conditions of this experiment. The asymmetric structure of the membrane consists of a porous substructure comprising the bulk of the polymer thickness, terminated by a thin osmotic skin.[18] Previous work[18,19] has yielded values near 60% moisture content at saturation for the membrane structure, more than three times the values of $M_h + M_s$ obtained in this study. The difference is believed to be due to capillary condensed water in the porous
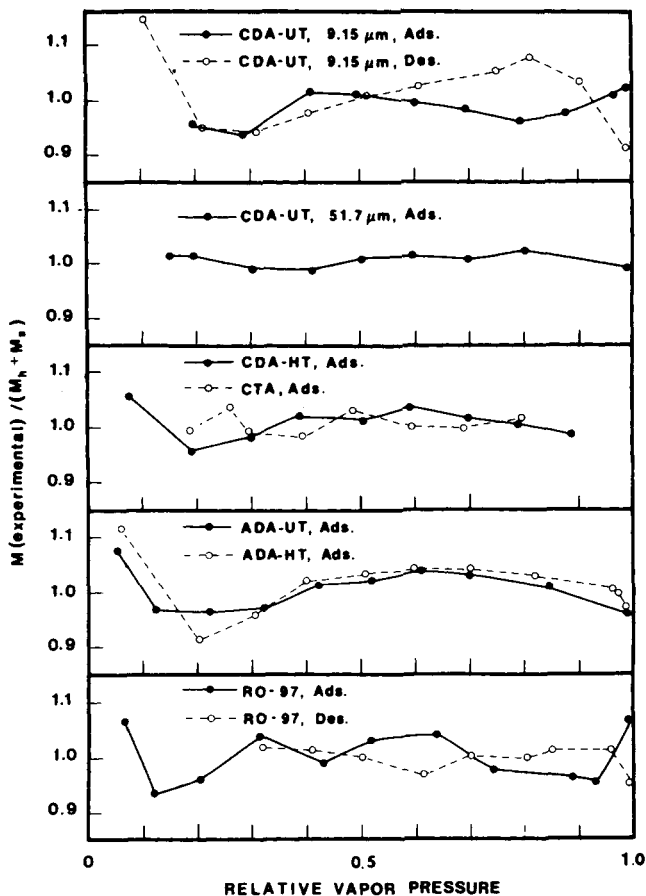
Fig. 4. Comparison of experimental isotherm points and Hailwood–Horrobin predictions.

substructure and consolidation of the substructure. This water is irreversibly removed from the membrane during the initial desorption reported in the present study since the experiment was begun in vacuum, while the previous study utilized never-dried material conditioned over sulfuric acid solutions at high humidity.[18] Using an NMR technique, Frommer and his co-workers came to the same conclusion.[19]

The effect of increasing the acetyl content from CDA to CTA is to reduce the amount of both hydrated (M_h) and dissolved (M_s) water (Table II). The value of 12.2% for the total water sorbed in the CTA film is comparable to previous results.[18] The effect of increasing the acetyl content is to reduce the amounts of water sorbed by replacing the highly polar hydroxyl groups with less hydrophilic acetate groups.[20]

Comparison of the data for cellulose acetate (CDA) and amylose acetate (ADA) in Table II shows lower values of both hydrated and dissolved water for amylose acetate. This is a reflection of the higher acetyl content of the ADA. Heating amylose acetate has no effect on the hydrated water M_h, but does reduce the water of solution M_s. This is in contrast to cellulose acetate in which heating was shown to have little effect on the sorptive properties. As has been shown

elsewhere, for the heating conditions used, CDA crystallized very little while, under the more severe condition (120°C, 20 min), ADA crystallized extensively.[21]

CONCLUSIONS

Experimental water sorption isotherms for amylose and cellulose acetates were discussed in terms of two theories: B.E.T. and Hailwood–Horrobin. The Hailwood–Horrobin theory was shown to fit the sorption isotherm throughout most of the relative vapor pressure region while the B.E.T. theory fitted the experimental isotherm up to 0.6 relative vapor pressure.

Heating cellulose acetate (70°C, 4 min) was shown to have little effect on sorption; but increasing the acetyl content (CTA) reduced both the hydrated, or surface-bound, water and the water of solution.

Amylose acetate sorbed less of both hydrated water and water of solution, and heating (120°C, 30 min) reduced the water of solution considerably. This was attributed to a higher degree of ordering, i.e., crystallinity, resulting in a decreased availability of sorption sites and surface area in the amylose polymers.

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