Water Permeation of Polymer Films. I. Polyimide

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Synopsis

The permeation of water has been measured through polyimide film over a range of thicknesses, temperatures, and relative humidities. The concentration of absorbed water was found to depend on the relative humidity and not on the temperature or sample thickness, reaching a maximum of one water molecule per repeat unit at 100% rh. This is discussed in terms of adsorption, with supporting data found in the surface-layer contribution to the permeability coefficient.

INTRODUCTION

DuPont Kapton polyimide, poly(4,4'-oxydiphenyl pyromellitimide), is a thermally and chemically stable film, useful in hostile environmental applications. In many of these applications, its use depends on its having a low permeation, particularly to water vapor.

In some applications, the polyimide may function as a dielectric. It is important to note, then, that while its ac properties are only minimally affected by water vapor,[1] its dc conductivity is substantially affected.[2] There may be other applications in which the functioning of the polyimide is subverted by the presence of ubiquitous water. Thus it is the purpose of this paper to evaluate the permeation properties of water through polyimide.

A previous study[3] evaluated the permeation of water through polyimide over a temperature range of 20–55°C and a relative humidity range of 25–100% rh. That study used only one thickness of film, ~127 μm. The present study not only extends the temperature range of 85°C, it also considers the effect of thickness, since permeation is a function of thickness.[4]

EXPERIMENTAL

The instrument used to follow the water permeation was a Dohrmann Envirotech Polymer Permeation Analyzer model PPA-1[5,6] which had been extensively modified. These modifications include a more stable power supply, larger diameter permeant delivery lines (to prevent pressurization at high flow rates), heatable permeant delivery and detector lines (to prevent condensation), continuous temperature monitoring of cells and detector, cell modifications for better sealing (concentric O-rings with in-between purge) and a new cell selector switch. The new switch permits two cells to equilibrate while the third is in use, effectively cutting experimental time by 60%.

Water vapor was supplied by a Dohrmann Envirotech Vapor Tech water generator, using deionized, distilled water having a resistance of at least 10^8 Ω cm.

Runs were carried out in the temperature range 30–85°C and in the range of

10–100% rh, although most experiments were carried out at 50% rh. Several runs were made under each condition, only after equilibration for several hours. Samples of 25.4, 50.8, and 127-μm Kapton were used, after having been cleaned with i-propyl alcohol to remove surface contaminants.

RESULTS

During the collection of this large body of data, two critical observations were made. First, at any constant relative humidity, the variation of the permeability coefficient P was well within experimental error over the temperature range used. For example, at 50% rh, P for 127-μm film decreases from 8.19×10^{-8} to 7.45×10^{-8} std cc cm/cm^2 sec cm Hg on going from 30 to 85°C. Such small variations may well be due to experimental errors, making it difficult to detect them accurately or to attribute too much meaning to them. Both diffusion coefficient D and solubility coefficient S values exhibit far more significant changes, making them easier to detect and more amenable to interpretation.

Second, irrespective of sample thickness and temperature, the water vapor concentration within the sample C was essentially constant at any constant relative humidity. Only at the temperature extremes of 30 and 85°C did any of the data deviate from this observation. These deviations, found to be due to experimental errors, were few in number, and this second critical observation became our criterion of data acceptance at the temperature extremes.

All the P, D, and S data fit Arrhenius equations:

$$P = P_0 \exp(-E_P/RT) \text{ std cc cm/cm}^2 \text{ sec cm Hg} \qquad (1)$$

$$D = D_0 \exp(-E_D/RT) \text{ cm}^2/\text{sec} \qquad (2)$$

$$S = S_0 \exp(-E_S/RT) \text{ std cc/cc cm Hg}, \qquad (3)$$

where P_0, D_0, and S_0 are the respective pre-exponentials, the E's are the appropriate activation energies (E_S is generally replaced by ΔH_S, the heat of solution[7]), R is the gas constant, and T is the absolute temperature. The values for the energies and pre-exponentials at 50% rh are found in Table I.

TABLE I
Permeation Values for Kapton at 50% rh

Parameter	Sample Thickness (μm)		
	25.4	50.8	127
P_0 (std cc cm/cm^2 sec cm Hg)	5.994×10^{-8}	3.458×10^{-8}	4.762×10^{-8}
E_P (kJ/mol)	1.07 ± 0.33	-1.28 ± 0.88	-1.34 ± 0.29
Statistical significance[a]	>0.9950	>0.9000	>0.9975
D_0 (cm^2/sec)	0.1367	0.03156	0.04518
E_D (kJ/mol)	46.42 ± 1.26	41.99 ± 1.84	42.24 ± 1.21
Statistical significance[a]	>0.9995	>0.9995	>0.9995
S_0 (std cc/cc cm Hg)	4.341×10^{-7}	1.100×10^{-6}	1.057×10^{-6}
E_S (kJ/mol)	-45.38 ± 1.26	-43.24 ± 1.93	-43.58 ± 1.21
Statistical significance[a]	>0.9995	>0.9995	>0.9995

[a] From both t-test and correlation coefficient.

Henry's law was followed; all the data were temperature independent, being accurately described by

$$C = 4.520 \times 10^{-4} \times \% \text{ rh} - 8.319 \times 10^{-4} \text{ g water/g polymer} \qquad (4)$$

with a statistical significance of >0.9995. A typical plot is seen in Figure 1.

Because of the previous study carried out on 127-μm Kapton,[3] the effect of relative humidity on that same thickness of film was extensively studied in the present case. Both P and D exhibited maxima near 50% rel. hum., while S remained virtually constant. The diffusion coefficient, for example, followed the equation[8]:

$$D/D^0 = 1 + C(a - bC) \qquad (5)$$

where D^0 is the value of D at zero C, and a and b are constants. A typical plot is seen in Figure 2, and typical a and b values are found in Table II.

The value of C at which D is a maximum is found by differentiating eq. (5) and setting the result equal to zero. This gives

$$\frac{dD}{dC} = a - 2bC = 0 \qquad \text{or} \qquad C = \frac{a}{2b} \qquad (6)$$

from which D has a maximum at $C = 0.0233$ g water/g polymer at 50°C and 0.0251 g water/g polymer at 70°C. From eq. (4), the maxima occur at 53 and 57% rh, respectively.
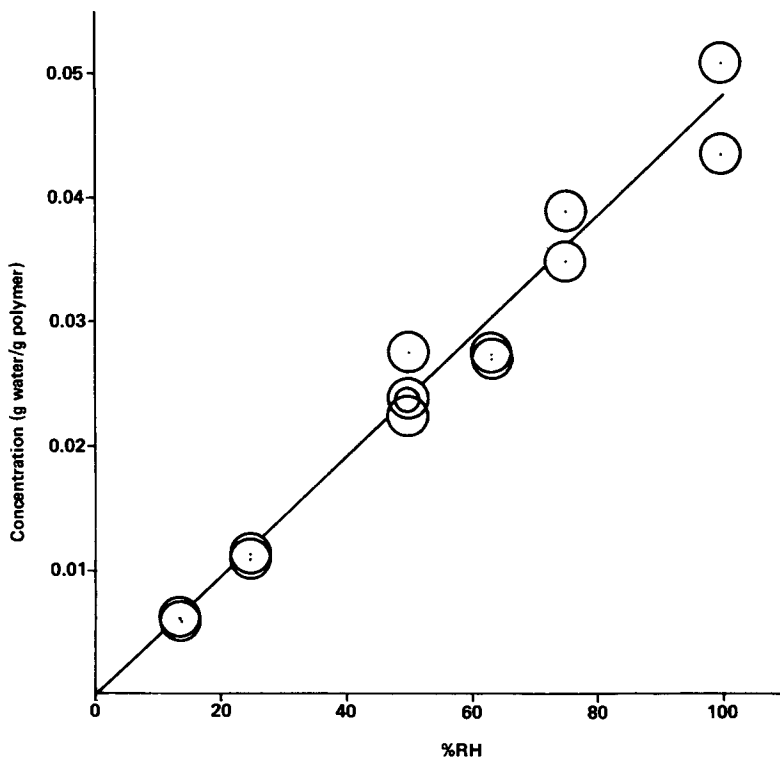

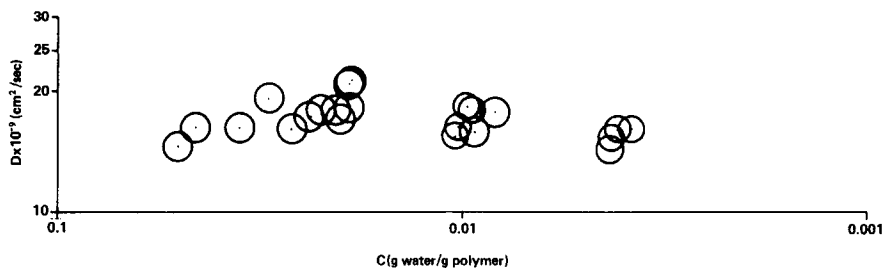Fig. 1. A Henry's law plot for 127-μm Kapton at 50°C.

Fig. 2. Variation of the 70°C diffusion coefficient through 127-μm Kapton with the concentration of absorbed water.

TABLE II
Constants[a] for the Humidity-Dependent Diffusion Coefficients of 5-Mil Kapton

T (°C)	D^0 (cm²/sec × 10⁻⁹)	a (g polymer/g water)	b (g² polymer/g² water)
50	6.558	7.99	172
70	14.42	21.9	436

[a] The D values predicted by these constants correlate with the experimental values to a statistical significance of >0.9995.

DISCUSSION

Permeability Coefficient

As indicated earlier, P (as well as D) is quadratically related to the concentration of absorbed water [see eq. (5)]. Interestingly, the maximum occurs near 0.024 g water/g polymer, or 0.51 mol water/mol polymer repeat units. The constancy of this number suggests an interaction between one water molecule and two polymer repeat units, which tends to limit the ability of further water molecules to permeate. Since the two repeat units must be on separate but close-lying chains and water is known to affect the molecular motions in Kapton,[1] this suggests interchain hydrogen bonding, which would present a low-energy barrier to the motion of further water molecules and might result in the maximum experimentally found. However, the diameter of a water molecule is less than 2.8 Å, while the closest interchain distance in Kapton is 4–5 Å,[9] making this explanation untenable.

The permeability coefficient data at 50% rh were found to fit the Arrhenius equation at each sample thickness. This is seen in Table I, where E_P is found to be positive in sign for the 25.4-μm samples and negative for both the 50.8- and 127-μm samples. The minor changes in P, over the experimental temperature range, make interpretation difficult. The 127-μm data, however, agree with the results of the previous study[3] in both magnitude and sign: there, P_0 was found to be 1.21 × 10⁻⁸ std cc cm/cm² sec cm Hg and E_P, −4.19 kJ/mol; these give P values which are a reasonable 22–28% (i.e., ~2 × 10⁻⁸ std cc cm/cm² sec cm Hg) lower than the present values.

Considering the permeation resistance of a sample to be the sum of surface layer and bulk resistances, it may be shown that[4]

$$1/P(L) = 1/P_\infty + (r_1 + r_2)/L \text{ cm}^2 \text{ sec cm Hg/std cc cm} \tag{7}$$

where $P(L)$ is the measured permeability coefficient at thickness L, P_∞ is that at infinite thickness, and $(r_1 + r_2)$ is the sum of surface-layer resistances.* Conceptually, $(r_1 + r_2)$ is the pressure necessary for the flow of unit flux.

The experimental data for the 25.4-, 50.8-, and 127-μm samples at 40, 50, and 70°C all fit eq. (7), with almost identical values of P and $(r_1 + r_2)$. An analysis of covariance, at the 95% confidence level, indicated that all the data could be represented by eq. (7) with $P_\infty = 9.041 \times 10^{-8}$ std cc cm/cm^2 sec cm Hg and $(r_1 + r_2) = 3.512 \times 10^{-4}$ cm^2 sec cm Hg/std cc. Table III compares the values predicted by eq. (7) with those predicted by eq. (1) at 50°C. This value of temperature was chosen for eq. (1) because P does, in fact, vary slightly with temperature, and 50°C appears to be the mean. The agreement in Table III indicates that eq. (7) may be used for prediction purposes when E_P is small and it is realized that a mean temperature is implied.

The variation of E_P with sample thickness is unexpected, particularly the change in sign below 50.8 μm. This may represent a situation in which the surface-layer thickness (3 μm) becomes appreciable when compared to the total sample thickness. Because of the uncertainties in the E values in Table I, it is presently unknown whether E_P changes abruptly between 25.4 and 50.8 μm or whether, as suggested by Figure 3, it is related to $1/L$.

Diffusion Coefficient

As with the permeability coefficient, the diffusion coefficient reached a maximum at a ratio of one water molecule per two repeat units, before decreasing. As indicated in the discussion on the permeability coefficient, a comparison of the closest interchain distance (4–5 Å) with the diameter of the water molecule (<2.8 Å) precludes interchain hydrogen bonding. Thus the water must be hydrogen bonded to only one of the chains, although it appears to be able to move from chain to chain.† Thus while plasticization by water increases molecular motions[1] and may cause the slight increase in D with increasing relative humidity,

TABLE III
Effect of Thickness on the Permeation of Water Vapor Through Kapton

| Thickness | P (std cc cm/cm^2 sec cm Hg $\times 10^{-8}$) | |
(μm)	Eq. (8)	Eq. (1) at 50°C
25.4	4.018	4.023
50.8	5.564	5.560
127	7.233	7.838

* The surface-layer resistance presumably arises from permeant immobilization at the sample surfaces.[10] As will be shown later, surface residence times for water are always less than 10^{-4} sec, making surface immobilization an improbable source for surface-layer resistance. However, microscopic examination of polyimide cast from N-methyl pyrrolidone solutions of its polyamic acid precursor (DuPont Pyre-ML RC-5057), cured according to the manufacturer's directions, and broken in tension, revealed a surface-layer contribution: down to a thickness of 3 μm, elongation and lateral shrinkage occurred in the region of the break as bulk material was drawn out. At 3 μm and below, no elongation occurred, distinguishing between surface and bulk contributions.

† The minimum energy of a hydrogen bond in polymers, E_{HB}, appears to be ~21 kJ/mol,[11–18] so that the fraction of free water molecules (= $\exp(E_{HB}/RT)$) is ~4 $\times 10^{-4}$ at 50°C. However, the residence time (= $10^{-12} \exp(E_{HB}/RT)$[19] is <3 $\times 10^{-9}$ sec, indicating that the water molecules flicker from point to point.
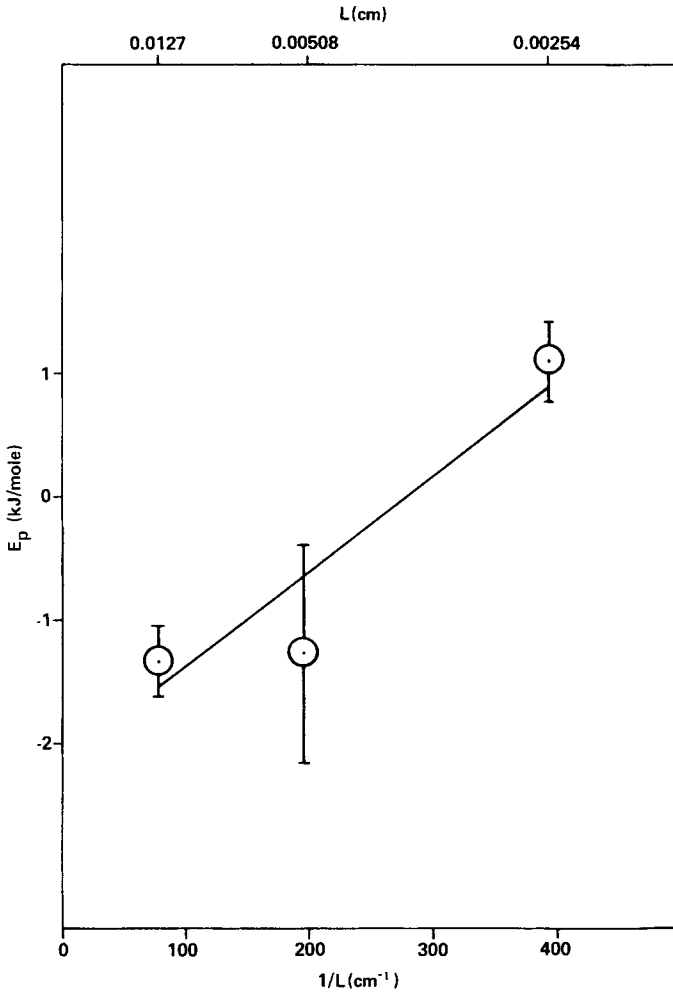
Fig. 3. Apparent variation of the activation energy for permeation with thickness.

the flickering back and forth of the absorbed water molecules may cause a barrier to the further diffusion of water above 50% rh.

The previous study[3] found D_0 and E_D to be 3.82×10^{-3} cm^2/sec and 35.2 kJ/mol, respectively, for 127-μm Kapton. While these values differ somewhat from the present values in Table I, they belie the close agreement of the two sets of data over the temperature range in which they overlap (30–55°C). This is brought out more clearly in Table IV, where both sets of values are within experimental error (estimated as ±10%).

The disagreement, more apparent than real, may be due to several causes: (1) a slight curvature of the Arrhenius plot, (2) the inherently larger error at lower temperatures, (3) calculation errors based on fewer data points, or (4) the difference in relative humidities (30% in Ref. 3 and 50% in the present case). The first cause may be discounted, since both sets of data give linear Arrhenius plots; the present study has a correlation coefficient of 0.9944 for 16 data points. The fourth point may similarly be discounted, since eqs. (4) and (5), as well as Figure

TABLE IV
Comparison of Diffusion Coefficient Predictions

T	Predicted D Values (cm^2/sec $\times 10^{-9}$)	
(°C)	Ref. 3	Present Work
20	2.09	a
30	3.36	2.41
40	5.25	4.11
55	8.42	8.62
85	a	31.5

[a] Outside experimental temperature range.

3 of Ref. 3,* predict a very small effect for the relative humidity difference, well within experimental error. Since their data were taken at lower temperatures and appear to be based on 6 data points, the second and third of the above causes cannot be discounted. This would favor our results.

Another reason for favoring the present results is concerned with the value of $\Delta S_D^{\ddagger}$, the entropy of activation for the diffusion process, calculated from Ref. 20, p. 524:

$$D_0 = \frac{2.7183 k T \lambda^2}{h} \exp\left(\frac{\Delta S_D^{\ddagger}}{R}\right) \qquad (8)$$

where λ is the mean jump distance and k and h are Boltzmann's and Planck's constant, respectively. Using $\lambda = 3$ Å (as in Ref. 3), the present data give $\Delta S_D^{\ddagger}$ (30°C) = 18.0, 25.0, and 10.9 J/mol K for the 25.4-, 50.8-, and 127-μm samples, respectively; in contradistinction, the previous study found $\Delta S_D^{\ddagger}$ (30°C) = −11.7 J/mol K for a 127-μm sample. Recalling that the water molecules do not form interchain bonds, which would be expected to reduce $\Delta S_D^{\ddagger}$, it seems to us that such an activated flow process should exhibit a positive $\Delta S^{\ddagger}$. There are two reasons for this: (1) a positive $\Delta S_D^{\ddagger}$ has been found for flow involving dipolar interactions between permeant and substrate (ref. 20, p. 505) and (2) a positive $\Delta S_D^{\ddagger}$ has been found for cases in which the lattice must distort for flow to occur (Ref. 20, pp. 538, 543).

Solubility Coefficient

Figure 4 shows that S is virtually constant with relative humidity, facilitating a comparison of the present study with the previous study on 127-μm Kapton.[3] Their values of S_0 and E_S (they use ΔH_S) are 3.17 $\times 10^{-6}$ std cc/cc cm Hg and −39.39 kJ/mol, respectively, in good agreement with the values in Table I.

As previously noted [see eq. (4)], C was temperature independent in the range of temperatures we considered, depending only on the value of the relative humidity. At 100% rh, eq. (4) gives a C value of slightly less than 0.05 g water/g polymer, which translates to 1.03 mol water/mol polymer repeat units. This is surprising in light of the fact that each polymer repeat unit has several dipoles, each of which might interact with the water dipole (four carbonyls, two imide

* Their Figure 3 indicates a monotonic rise of D with % rh, while the present data [eq. (4) and Fig. 2] indicate a small maximum at ~50% rh. In both cases, however, ΔD between 30 and 50% rh is <0.5 $\times 10^{-9}$ cm^2/sec.
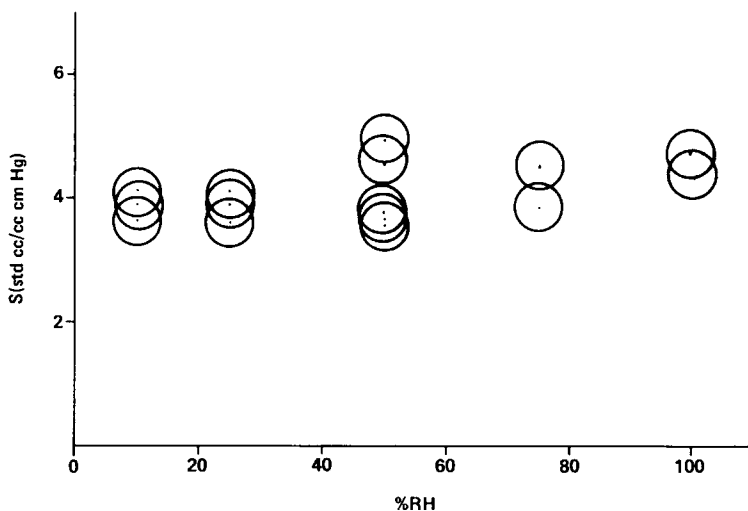
Fig. 4. Sorption isotherm for 127-μm Kapton at 70°C.

nitrogens, and an ether oxygen). The only molecular motions affected by the presence of water[1] are those involving localized out-of-plane bending of the carbonyls, accommodated by a flexible ether linkage. Since these involve two imide groups and only one ether linkage per repeat unit, and since there is at most one molecule of water associated with each repeat unit, the data suggest that the water molecule is associated with the ether linkage. This appears reasonable, since group dipole moment data[21] suggest that the carbonyl dipole moments in the imide group are opposed in orientation, tending to give a resultant moment significantly lower than that of the ether linkage.

The numerator of the exponential in eq. (3) is generally taken to be the heat of solution ΔH_S, in a process visualized as the condensation of the vapor onto the sample surface, followed by solution of the condensed penetrant into the polymer:[22–24]

$$\Delta H_S = \Delta H_{\text{cond}} + \overline{\Delta H}_{\text{mix}} \qquad (9)$$

where ΔH_{cond} is the molar heat of condensation, obtained from the process

$$H_2O \text{ (vapor)} \rightarrow H_2O \text{ (liquid)} -\Delta H_{\text{cond}}, \qquad (10)$$
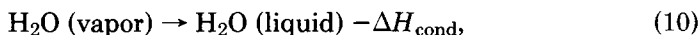
and $\overline{H}_{\text{mix}}$ is the partial molar heat of penetrant–polymer mixing.

The process in eq. (10) does not seem to apply to the present situation, since preliminary sorption-balance studies indicate a Fickian process (i.e., Δ mass $\propto t^{1/2}$) to at least 85% of the total absorption; further, Figure 4 is characteristic of a Brunauer type I (i.e., Langmuir) isotherm. Together they indicate that water absorption onto Kapton is no more than one monolayer thick. That is, rather than the process outlined in eq. (10), we have

$$H_2O \text{ (vapor)} \rightarrow H_2O \text{ (adsorbed)} - \Delta H_{\text{ads}}, \qquad (11)$$

where ΔH_{ads} is the molar heat of adsorption. Since, $\Delta \overline{H}_{\text{mix}}$ is expected to be

negligibly small for condensible vapors like water,* it is our contention that E should more properly be replaced by ΔH_{ads} in the present case, rather than by ΔH_{cond}.

A further reason for assuming that E_S is ΔH_{ads}, and not ΔH_{cond}, is that ΔH_{cond} is not constant over the temperature range studied. Steam tables show it to decrease from 43.7 kJ/mol at 30°C to 41.4 kJ/mol at 85°C. Table I shows that the E_S values do not vary, as indicated by the extremely high statistical significances of the linear Arrhenius plots. Such a constancy of E_S is consistent with eq. (10), in light of the fact that the dielectric data[1] indicate no major variations in the structural motions of the polyimide in this temperature range.

The residence time τ of a molecule on a surface is related to E_S by[19]

$$\tau = 10^{-12} \exp(-E_S/RT) \text{ sec} \qquad (12)$$

For the 25.4-, 50.8-, and 127-μm samples, τ (30°C) = 6.52, 2.80, and 3.19 $\times$ 10^{-5} sec, respectively. These low values are consistent with monolayer adsorption, supporting our contention that E_S is equal to ΔH_{ads} in the present case.

CONCLUSIONS

Water permeation through polyimide initiates by monolayer adsorption. Solubility coefficient data indicate that the enthalpy of adsorption is the principal contributor to the E_S term. The constancy of ΔH_{ads} over the temperature range employed is reflected in the temperature and thickness independence of Henry's law in the present case. Permeability coefficient data indicate a surface-layer resistance, in addition to the expected effect of the bulk; tensile data indicate that the surface layers are each 1.5 μm thick.

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* We attempted to calculate $\overline{\Delta H}_{\text{mix}}$, using Hildebrand's equation[25]:

$$\overline{\Delta H}_{\text{mix}} \approx \overline{V_1}(\delta_1 - \delta_2)^2 \, \theta_2^2$$

where $\overline{V_1}$ is the partial molar volume of penetrant, δ_1 and δ_2 are the solubility parameters of penetrant and polymer, respectively, and θ_2 is the volume fraction of polymer. The solubility parameter for Kapton was estimated[26] as 56.1 (J/cc)$^{1/2}$, giving $\overline{\Delta H}_{\text{mix}} > 110$ kJ/mol at 50% rh. Clearly the assumptions leading to Hildebrand's equation[27] do not hold in this case, and the equation must be modified.[27]

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