

Water Permeation of Polymer Films. II. Dual-Mode Absorption in Teflon FEP

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Synopsis

DuPont Teflon FEP has been shown to permeate water vapor through a dual-mode process: adsorption followed by permeation. A model is proposed for this process based on the interactions of condensable gas molecules with themselves and with the polymer surface. This model appears to have general applicability.

INTRODUCTION

Dual-mode absorption¹ is exemplified by a Henry's law plot shown schematically in Figure 1. A process which occurs at low pressures saturates at higher pressures and is superimposed on a Henry's law process. The process that saturates is usually presented in terms of a Langmuir isotherm, so that the superimposed processes may be written as

$$C = C_L + C_H \quad (1)$$

where C_L is the concentration of material sorbed through the Langmuir isotherm and C_H is that which follows Henry's law.

When the pressure is presented as relative humidity, the Langmuir process may be written as

$$C = \frac{C'_L \times b \times \%R.H.}{1 + b \times \%R.H.} \quad (2)$$

where C'_L is usually called the saturation constant (the maximum concentration of the Langmuir isotherm) and b is termed an affinity constant. Similarly,

$$C_H = k \times \%R.H. \quad (3)$$

where k is the solubility coefficient. Thus,

$$C = \frac{C'_L \times b \times \%R.H.}{1 + b \times \%R.H.} + k \times \%R.H. \quad (4)$$

At sufficiently low relative humidity, where $b \times \%R.H. < 1$,

$$C = (C'_L \times b + k) \%R.H. \quad (5)$$

Similarly, at high relative humidity, where the Langmuir isotherm has saturated, $b \times \%R.H. > 1$ and

$$C = C'_L + k \times \%R.H. \quad (6)$$

That is, such plots are linear at the two extremes of pressure.

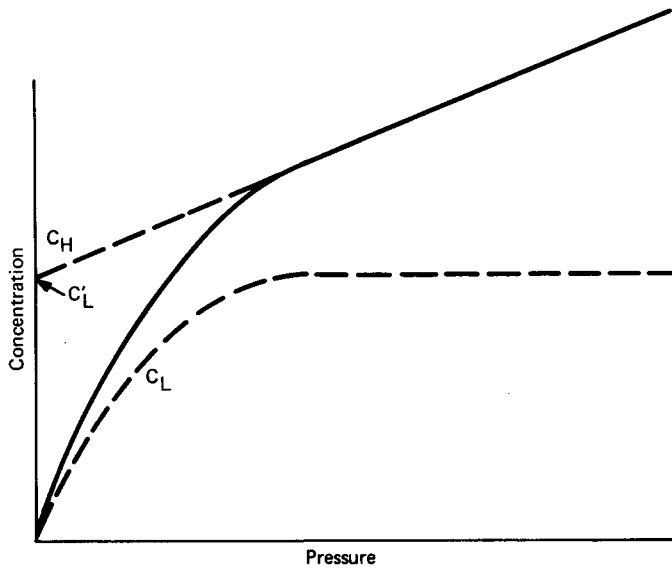


Fig. 1. Stylized Henry's law plot of dual-mode absorption.

We have been concerned with water permeation through Teflon FEP and, while these results will be discussed in a future paper, several things cause us to believe that we are experiencing dual-mode absorption. First, the solubility coefficient (and therefore the concentration of sorbed water) measured early in a run is invariably less than that measured later in the same run. Second, Henry's law plots of both sets of data, in Figure 2, show linearity but do not intercept the origin in either case.

EXPERIMENTAL

Samples of extruded DuPont Teflon FEP type 100A, 25.4 μm thick, were obtained commercially. Their water vapor permeation parameters were measured in a Dohrmann Envirotech polymer permeation analyzer Model PPA-1, modified as previously described.²

The recommended procedure for calculating the permeation parameters³ was used. This means that the permeation coefficient P was obtained from the total instrument signal, while the diffusion coefficient D , the solubility coefficient S , and the concentration of sorbed water C were obtained from two sets of data: X_1 was obtained from data between 10% and 40% of the permeation process and X_2 , from data between 40% and 70% of the permeation process. While X_1 and

TABLE I
A Comparison of Diffusion and Solubility Coefficients at 50% R.H.

$T, ^\circ\text{C}$	$D_1 \times 10^{-8}$ ^a	$D_2 \times 10^{-8}$ ^a	S_1 ^b	S_2 ^b
30	3.78	3.06	0.0830	0.103
55	5.85	4.61	0.0996	0.126
80	5.98	4.44	0.130	0.174

^a In units of cm^2/sec .

^b In units of std cc/cc cm Hg.

X_2 were within experimental error in the case of water permeation through DuPont Kapton polyimide film² and through many other materials as well,^{3,4} this was not true in the present case.

RESULTS

Depending on the conditions of the experiment, D_1 was ~25%–35% higher than D_2 , with the reverse being true for S_1 and S_2 . Typical values are found in Table I.

Values of C , obtained at 55°C, are plotted in Figure 2, from which it was found that

$$C_1 = 2.694 \times 10^{-6} \%R.H. + 3.836 \times 10^{-5} \text{ g water/g polymer} \quad (7)$$

and

$$C_2 = 3.193 \times 10^{-6} \%R.H. + 5.882 \times 10^{-5} \text{ g water/g polymer} \quad (8)$$

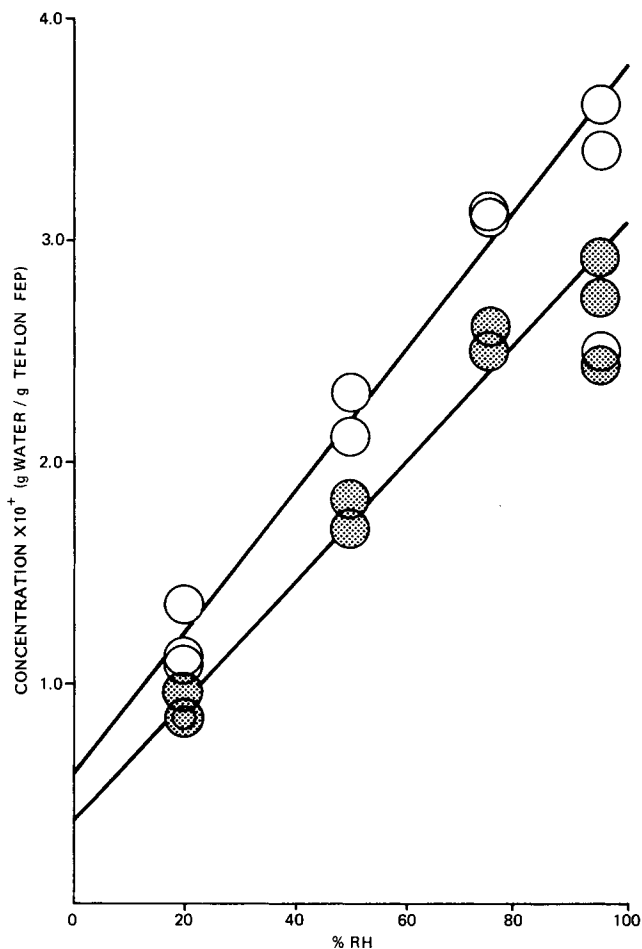


Fig. 2. Henry's law plots of C_1 and C_2 at 55°C.

both straight lines had statistical significances of >0.9995 .* The intercepts of these equations are C'_{L1} and C'_{L2} , respectively, indicating an increase of $\sim 53\%$ in the Langmuir saturation constant as the permeation proceeded.

DISCUSSION

C_L' is the maximum concentration of the Langmuir adsorption isotherm. It may be used to calculate the actual number of molecules on the surface: since the density of Teflon is 2.15 g/cc, a gram of this material has a volume of 0.465 cc. A 25.4- μm -thick sample would, therefore, have a surface area of 183 cm^2/g . C'_{L1} indicates that this area contains 3.836×10^{-5} g water = 1.28×10^{18} molecules, or 0.70 molecules/ \AA^2 .

Now, water has a molar volume of ~ 18 cc, which means that each molecule occupies a volume of $\sim 30 \text{\AA}^3$. Assuming isotropy, each molecule occupies an area of $\sim 9.65 \text{\AA}^2$. Thus, to satisfy the requirements of C'_{L1} requires $9.65 \times 0.70 = 6.8$ monolayers. Similarly, C'_{L2} requires 10.5 monolayers. Since Langmuir isotherms are considered to be composed of only one monolayer, we are not dealing with a Langmuir isotherm, per se.

In retrospect this is not surprising, since water is known to cluster in the bulk liquid in groups having an average of 5.5 molecules.⁵⁻⁷ In the vapor phase, however, water association is insignificant,⁸⁻¹⁰ so that clustering of the adsorbate could occur only during adsorption.

The standard errors of the estimates of C_1 and C_2 are $\pm 1.256 \times 10^{-5}$ and $\pm 1.501 \times 10^{-5}$ g water/g polymer, respectively, so that one might argue that C'_{L1} and C'_{L2} are in fact identical, with an average adsorbate cluster size of some 8.7 molecules. That is, one may be dealing with a Langmuir-like adsorption of a monolayer of water clusters.

This argument may be supported by considering the residence time of water on the surface. Although a fuller account will be given in a future publication, we have found that, at 50% R.H., E_{S1} and E_{S2} are both near zero. It was argued in an earlier paper that E_S is in fact ΔH_{ads} , the molar heat of adsorption, and the present data support this: since $C_H = 0$ at $t = 0$ and is substantially smaller than C_L for the first 20–30% of the permeation process, it is clear that permeation involves an initial adsorption of water onto the polymer surface. These values of E_S may be used to calculate the residence time τ of the molecule on the surface¹¹:

$$\tau = 10^{-12} \exp(-\Delta H_{\text{ads}}/RT) \text{ sec} \quad (9)$$

The values obtained for τ_1 and τ_2 are both near 10^{-12} sec. Such short times are difficult to reconcile if one considers the adsorbed water layers to be independent of each other. Thus, the data indicate that water forms clusters on absorption and that the clusters are desorbed in $\sim 10^{-13}$ sec.

Although this value is surprisingly low, it does indicate why water permeates so slowly through Teflon: since molecular motions occur on the order of 10^{-12} sec, water will be desorbed unless it fortuitously falls into a channel between the Teflon chains and gains entrance into the bulk. In contrast, $\tau \approx 10^{-5}$ sec for Kapton,² so that water is resident on its surface for $\sim 10^7$ molecular motions, with

* An analysis of covariance, to the 95th percentile, indicated that the two lines were not parallel, nor did a common regression line exist.

an increased probability of a favorable channel opening nearby for permeation; coupled with a far greater water solubility than that for Teflon,[†] this leads to a larger water permeation for Kapton.

The longer residence time and higher C value for Kapton indicate a strong dipole-dipole interaction between the polymer and the water immediately adjacent to it. Thus, the water will be less prone to form clusters than in the case of Teflon, where water-polymer interactions are minimal. That is, the thickness of the adsorbed water layer will depend on the magnitude of ΔH_{ads} .

The process we envision may be modeled on a simple Langmuir adsorption process, which is modified so that *some* of the adsorbed molecules may then continue to permeate. Consider S surface sites, whose occupancy by a monolayer of water clusters of unspecified size is pressure dependent:



A fraction Ψ ($\ll 1$) of the water molecules at the adsorbed sites may then permeate through the film:



Since $dS_{\text{ads}}/dt = 0$,

$$k_1 p S_{\text{unoccupied}} = (k_2 + k_3 \Psi) S_{\text{ads}} \tag{12}$$

Further, we define

$$\frac{S_{\text{ads}}}{S_{\text{total}}} = \theta = \frac{k_1 p}{k_1 p + k_2 + k_3 \Psi} = \frac{bp}{bp + 1} \tag{13}$$

where

$$b = \frac{k_1}{k_2 + k_3 \Psi} = k_1 \tau^\dagger \tag{14}$$

Because the amount permeating per unit area is the flux F , one may write

$$F = k_3 \Psi S_{\text{ads}} = k_3 \Psi \theta S_{\text{total}} \tag{15}$$

where the flux is seen to depend on coverage.

The application of this model to the present study may be tested in the following way: Because

$$F = \frac{pP}{l} \tag{16}$$

where l is the thickness, the flux may be calculated from the permeation coefficient. Since θ approaches a constant maximum as p increases, a plot of F versus %R.H. should show this. Such a plot is seen in Figure 3, where F clearly levels off with increasing pressure.

Now, Figure 3 may be considered a general plot for permeation processes, with

[†] From eqs. (7) and (8), C_{H_1} and C_{H_2} are, at 100% R.H., 2.694×10^{-4} g water/g polymer (= 1.5×10^{-3} moles/water/mole polymer repeat unit) and 3.193×10^{-4} g water/g polymer (= 1.8×10^{-3} moles water/mole polymer repeat unit), respectively. For Kapton,² $C = 4.52 \times 10^{-2}$ g water/g polymer (= 1 mole water/mole polymer repeat unit).

[‡] Note that the rate constant for desorption, $k_2 + k_3 \Psi$, is equal to τ^{-1} .¹¹

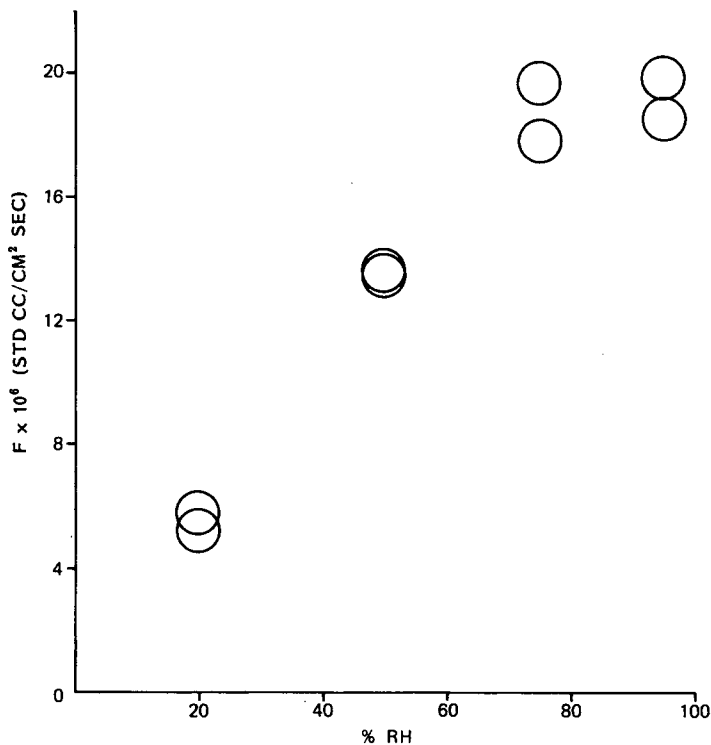


Fig. 3. Plot of the variation of F with relative humidity at 55°C.

F either reaching a maximum within the pressure range or tending to reach the maximum. The extent to which this is accomplished depends, in the present model, on the magnitude of b , the affinity constant, which is itself a ratio of rate constants. Further, the magnitude of the flux is related to Ψ which is in turn related to E_S (through τ). Thus, the model presented in eqs. (10)–(14) may have more general applicability.

In the case of Kapton, not only will the thickness of the adsorbed layer be less, due to a greater water-polymer interaction, but the value of b ($= k_1/k_2 + k_3\Psi$) will also be less because of the increased value of $k_3\Psi$. Taken together, they indicate less complete surface coverage by a thinner layer than in the case of Teflon.

Our model is based on the interactions of condensable gas molecules with themselves and with the polymer surface and appears generally applicable to such cases. Even the dual-mode Henry's law plot of benzene permeating through poly(ethylene terephthalate)¹² may be thought of in terms of π - π interactions.¹³ However, the dual-mode sorption of methane into polystyrene,¹⁴ for example, indicates that there must be at least one other mechanism for this phenomenon.

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