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The Use of Fourier Transform Infrared (FT-IR) Spectroscopy to Determine the Diffusion Coefficients of Alcohols in Polydimethylsiloxane

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A variable long path gas cell was used to measure the sorption of organic vapors by a polymer slab. Unfilled polydimethylsiloxane (PDMS) slabs were cast and used to study the sorption of a series of aliphatic alcohols. The PDMS slab was suspended in the gas cell and exposed to low relative pressures of an alcohol vapor. The sorption rate of the alcohol vapor by the PDMS slab was obtained by measuring the decrease in the amount of free diffusant in the gas cell. The diffusion coefficients of the alcohols in the PDMS slab were then calculated from the curves of amount of diffusant sorbed versus time. The results show that the values of the diffusion coefficients at nearly infinite dilution, D_0, for methanol, ethanol, 1-propanol, and 1-butanol are 1.01×10^{-5}, 0.61×10^{-5}, 0.54×10^{-5}, and 0.33×10^{-5} cm^2/sec, respectively. The isotherms for the sorption of the alcohols by the PDMS slab were also constructed from the data.

KEY WORDS: diffusion coefficient; Fourier transform infrared (FT-IR) spectrometer; aliphatic alcohols; polydimethylsiloxane.

INTRODUCTION

The permeation of environmental pollutants through the skin is a current subject of concern. Although the concentrations of many of these hazards in the air are low, a high permeability might result in significant adverse health effects. It was of interest to develop a technique that would allow a relatively rapid assessment of the ability of vapors present in the parts per million range to transport into either skin or polymeric membranes.

The transport of a relatively noninteracting diffusant in a polymer above its glass transition temperature almost always follows the classical behavior predicted by Fick's second law, assuming that the diffusion coefficient is constant. An increase in the polymer–diffusant interaction leads to increased sorption of the diffusant with the result that the diffusion coefficient often becomes concentration dependent. There are three principal methods for measuring diffusion coefficients in polymers. These methods are gas permeation (1–4), sorption (5–11), and radiotracer (12–14).

The sorption method is probably the most widely used method to measure the diffusion coefficient in a gas–polymer system. A polymer film is equilibrated with a certain pressure of the vapor of the penetrant. The gain in weight of the film is measured as a function of time by direct weighing of the polymer (5,6) or by observing the distention of a quartz spring holding the polymer (7–11). Use of either of these techniques for very low vapor concentrations is frequently difficult.

A spectroscopic variation of the sorption method was developed which employed a Fourier transform infrared (FT-IR) spectrophotometer. This method is sensitive to very low P/P_0 values and does not involve perturbing the system to perform a measurement. A secondary advantage of this technique is that the diffusion coefficients obtained are reasonable approximations of the diffusion coefficients at infinite dilution. Polydimethylsiloxane (PDMS) was selected to serve as the model polymeric material since it has been well characterized.

MATERIALS AND METHODS

Materials

The aliphatic alcohols used were methanol (Mallinckrodt Specialty Chemicals Co., Paris, KY; Lot 3016 KHCD), ethanol (Midwest Grain Products, Pekin, IL; Lot C01116), 1-propanol (Fisher Scientific, Fair Lawn, NJ; Lot 911529), and 1-butanol (EM Science, Gibbstown, NJ; Lot 30214038).

Synthesis of the PDMS Membrane

A mixture of 43.52 g of liquid polydimethylsiloxane, hydroxy terminated, MW 36,000 (Scientific Polymer Products, Inc., Ontario, NY; Lot 4), and 1.49 g of tetrapropylorthosilicate (Aldrich Chemical Company Inc., Milwaukee, WI; Lot 1219BJ) was thoroughly blended. About 9 drops of stannous octoate (Pfaltz & Bauer, Inc., Lot S08480) was added and mixed in well. The preparation was then put in the vacuum oven for about 5–10 min to eliminate air bubbles. The PDMS slab was cast using a glass plate with four fixed glass sides. The slab was allowed to cure at room temperature (20–24°C) for at least 24 hr prior to use.

The thickness of the PDMS slab was measured by placing the slab between two sheets of paper. The thickness of the combined paper and slab was measured using a micrometer (Craftsman Micrometer, Sears, Roebuck and Co., Chicago, IL) at 20 predetermined points. The thickness of the two sheets of paper was then measured and subtracted from the total thickness to determine the slab thickness. The slab used for these experiments was 9.50 cm long, and 6.50 cm wide and had a mean thickness of 0.518 cm (standard deviation, 0.003 cm).

Experimental Procedures

The sorption system was composed of the gas inlet system (I), the gas cell (II), and the gas outlet system (III). A diagram of the sorption system is shown in Fig. 1. Stainless-steel tubing and stainless-steel valves were used throughout the inlet system, whereas rubber tubing and high vacuum stopcocks were used for the outlet system.

The gas cell (Spectra Tech, Inc., Stamford, CT) was set to have a pathlength of 2.12 m. The gas cell and accompanying manifold were then mounted on a Nicolet 5-DXB spec-

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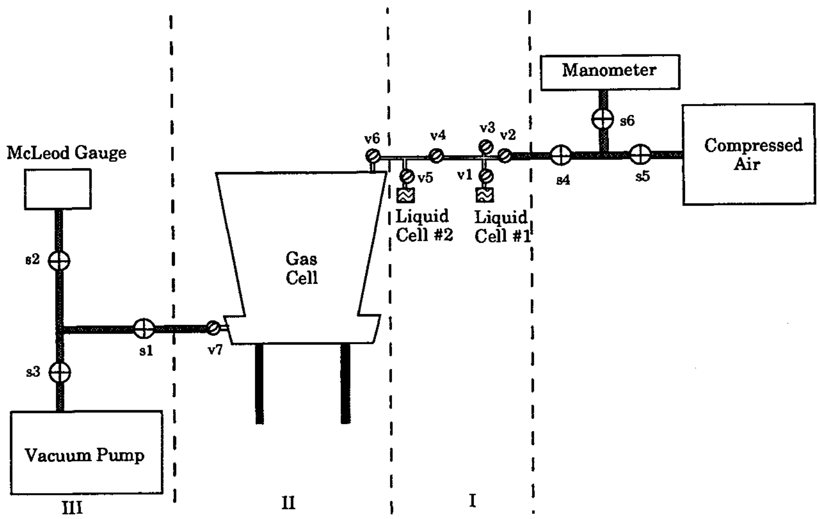

Fig. 1. The sorption system for determining the diffusion coefficients of alcohol vapors in a polydimethylsiloxane membrane. (I) The inlet system; (II) the long path gas cell; (III) the outlet system.

trophotometer (Nicolet Instrument Corp., Madison, WI) such that the external mirrors for the gas cell were inside the sample compartment. The desired amount of a particular liquid alcohol was placed in liquid cell 1, while valve v1 was closed. With valves v1, v2, v3, and v5 closed, v4, v6, and v7 open, and stopcocks s1, s2, and s3 open, the vacuum pump was turned on to evacuate the air from the gas cell. When the pressure was less than 1 mm Hg, valve v7 was closed and the vacuum pump was turned off. The background spectrum was obtained from the coaddition of 10 scans at 4-cm^{-1} resolution and a detector gain of 1. Valve v1 was opened and spectra of the test vapor were collected against the vacuum background at appropriate intervals of time. Usually, a spectrum was taken every minute for 5 min, at intervals of 5 min for the next 55 min and at intervals of 15 min for the last 4 hr (the total data acquisition period was 5 hr). These spectra were used as a control for absorbance change with time and were also used to construct a calibration plot. The experiment was repeated a second time, as described above, except that a 6.50 × 9.50 × 0.518-cm PDMS slab was placed inside the gas cell but out of the path of the IR beam. Importantly, both sides of the polymer slab had maximum exposure to the vapor. The room temperature was 21 ± 0.5°C, with 1°C being the largest temperature difference occurring between runs. Various amounts of each alcohol were evaluated in the same manner. The maximum amount of liquid that was placed in the liquid cell was limited by the requirement that the IR peak used for analysis have an absorbance of 0.7 or less. The amounts of methanol used were 20, 30, 40, 50, 60, 70, 80, and 90 μL, those of ethanol were 5, 10, 20, 30, 40, 50, 60, and 70 μL, those of 1-propanol were 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 μL, and those of 1-butanol were 5, 10, and 15 μL. The low vapor pressure of 1-butanol was responsible for the limited number of vapor concentrations of this liquid. For the pressure of the alcohol to be known, it was necessary for the entire volume of alcohol to vaporize into the known volume of the gas cell and manifold. Although there were no differences in D_0 values between slabs when slight differences in thickness were accounted for, a single PDMS slab was used throughout the reported experiments to decrease the potential error resulting from slab variation. The PDMS slab was, however, kept under vacuum overnight between the runs to ensure that there was little or no diffusant remaining from the previous run.

The total volume of the gas cell and the inlet system was 3.532 L. This volume was experimentally determined using a vessel of known volume (1.096 L) that was temporarily attached to the system, a tank of CO_2 gas, and the relationship $P_1V_1 = P_2(V_1 + 1.096)$.

Analysis of the Alcohol Vapor Spectra

The alcohol vapor spectra from the control runs and from the runs with the slab were evaluated using integrated absorbance. The selected peak regions for methanol, ethanol, 1-propanol, and 1-butanol were 3750.0–3626.0 cm^{-1} (O–H stretching), 1276.5–1250.0 cm^{-1} (C–O stretching), 1253.0–1194.0 cm^{-1} (C–O stretching), and 1104.0–1015.5 cm^{-1} (O–H bending), respectively.

RESULTS AND DISCUSSION

The spectra of the alcohol vapors in the absence of the PDMS slab were evaluated using the integrated absorbance of the selected medium intensity peak (C–O stretching or O–H bending). Since these bands in the methanol spectrum were of a high intensity, the O–H stretching band was used for the analysis. The values of the integrated absorbances of the selected peak were plotted against the amounts of alcohol added initially. The integrated absorbance values were the averages of several measurements taken after an isotropic distribution of vapor had been achieved. All calibration plots exhibited good linearity, with correlation coefficients better than 0.999. This linearity was to be expected since the integrated absorbance can be viewed as the summation of all of the individual Beer–Lambert law relationships existing over the peak region. The calibration equations were used to calculate the amount of alcohol vapor sorbed by the PDMS slab during the sorption process.

It was assumed that the adsorption process was rapid relative to the subsequent diffusional transport into the polymer slab. On this basis, the rate-limiting step for the loss of alcohol vapor was the diffusional process. Using the calibration equation, the amounts of alcohol vapor in the cell with and without the PDMS slab were calculated. The difference in these two calculations was then the amount of alcohol that had entered the PDMS slab. The equilibrium amount of alcohol in the slab (M_e), which would theoretically be obtained only at infinite time, was calculated from the average value of the sorbed amounts after the time at which the measured maximum value became constant. The fractional amount sorbed by the slab (M/M_e) was then calculated.

Since the sorption of the alcohol vapor by the PDMS slab was determined from the decrease in the amount of free alcohol vapor in the gas cell, the experimental procedure represented the case of diffusion from a limited volume of diffusant. This experimental model is described by the following equation (15,16):

$$\frac{M}{M_e} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(\frac{-Dq_n^2 t}{L^2}\right) \qquad (1)$$

where M is the total amount of diffusant in the slab at time t, M_e is the equilibrium amount of diffusant in the slab at $t = \infty$, the slab has a thickness of $2L$, and D is the diffusion coefficient (assumed to be constant). The values of q_n in Eq. (1) are the nonzero positive roots of

$$\tan q_n = -\alpha q_n \qquad (2)$$

where α is the ratio of the volumes of the vapor and the slab. That is, $\alpha = a/KL$, where K is a partition factor and a is half of the volume of the gas cell. The variable α can also be calculated from the fractional amount of diffusant sorbed by the slab in the final equilibrium state, F, as in Eq. (3):

$$F = \frac{M_e}{2aC_0} = \frac{1}{1+\alpha} \qquad (3)$$

where C_0 is the concentration of diffusant in the cell at initial time.

Since M/M_e was determined at various times, t, the value of the diffusion coefficient, D, could be readily calculated from the diffusion equation since all other variables were known. In this study, the value of α was calculated from the fractional amount sorbed at equilibrium, F, where F was the ratio of M_e and the amount of alcohol used initially.

It was assumed for analysis purposes that significant transport into the slab only occurred through the two large planar surfaces (combined surface area of 123.5 cm^2). This would seem to be valid since the total edge area of about 16 cm^2 constituted only 12% of the total surface of the slab. Furthermore, the distance to the center of the slab from an edge was so large that this pathway was assumed to make a negligible contribution to the overall rate of sorption.

It was found that the difference in the value of the diffusion coefficient calculated using six terms versus seven terms of the series in Eq. (1) was less than 0.5%. Therefore, six terms were used in the calculation of the diffusion coefficients. The fractional amount of diffusant sorbed (F) in each individual run differed from that in the other runs. As a result, the values of α and q_n, which were calculated from F, also differed between runs. A particular set of values was thus unique to each individual data set. For example, the equation for the sorption of 1-propanol (30 μL added initially) by the PDMS slab was

$$\begin{aligned} M/M_e = 1 - (&0.60 * e^{-68.91Dt} + 0.17 * e^{-370.90Dt} \\ &+ 0.071 * e^{-960.52Dt} + 0.038 * e^{-1843.69Dt} \\ &+ 0.023 * e^{-3021.18Dt} + 0.016 * e^{-4492.10Dt}). \end{aligned} \qquad (4)$$

Figure 2 shows the curve fitting for the sorption data for 1-propanol (30 μL added initially) obtained using Eq. (4). The correlation coefficient for the fit was 0.993. The sorption plots for all four alcohols indicated that the sorption processes were Fickian since all sorption plots showed linearity in their initial regions (Fig. 3).

The values of the diffusion coefficients for various initial amounts of methanol, ethanol, 1-propanol, and 1-butanol obtained by this method are presented in Table I. It can be seen that the values of the diffusion coefficients of ethanol, 1-propanol, and 1-butanol are relatively constant and are independent of the initial diffusant concentration. Since the sorption of alcohols was observed at a low relative pressure, the average of these values for each alcohol can be considered to be the diffusion coefficient for the infinite dilution case (D_0).

The diffusion coefficient for methanol does not seem to be constant. For initial amounts of 20–50 μL, the value of D seems to have a relatively constant value. For initial amounts of 60–90 μL, D seems to have a relatively constant but lower value. The same behavior has been reported by Barrie and Machin (17) for the diffusion of methanol in polydimethylsiloxane polymer. The unusual behavior observed here, where the diffusion coefficient decreases with increasing concentration, occurs for low molecular weight diffusants that exhibit a high degree of hydrogen bonding, such as water and methanol (7,8,17,18). The sorbed molecules associate within the polymer as the concentration increases such that the diffusant becomes less mobile. Methanol, which is strongly sorbed, shows a tendency to associate at fairly low relative pressures (17). When the initial amount of methanol added exceeded 50 μL, the diffusion coefficient decreased, seemingly indicating that association was occurring. The D_0

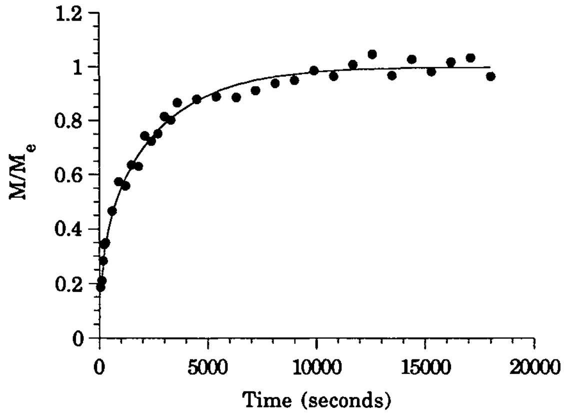

Fig. 2. Sorption plot of M/M_e versus time for 1-propanol (30 μL) in the PDMS membrane. The circles represent the experimental data and the line is the fitted curve obtained using Eq. (4). The correlation coefficient for the fit is 0.993.

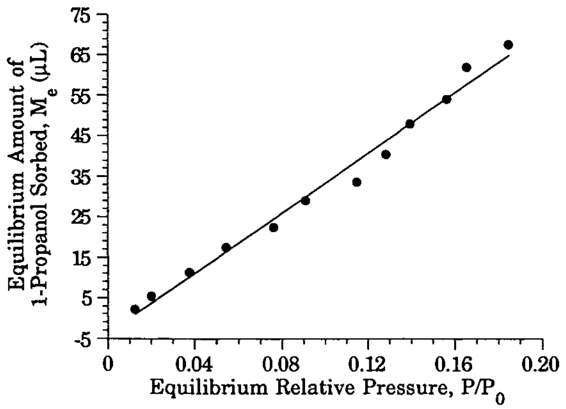

Fig. 3. Isotherm of the equilibrium amount of 1-propanol sorbed by the PDMS membrane versus the equilibrium relative pressure. The correlation coefficient for the linear fit is 0.993.

value for methanol was therefore determined by using the average value of the diffusion coefficients obtained for initial amounts of 20 through 50 μL.

Table II shows a comparison of the values of D_0 obtained by this method to those from the literature. The value of D_0 for methanol is in agreement with the value obtained by Barrie (19), and the value of D_0 for ethanol agrees with those obtained by Radovanovic *et al.* (20) and by Okamoto *et al.* (21). The D_0 value for ethanol given by Radovanovic *et al.* (20) was estimated by ratioing the diffusion coefficient values of methanol and ethanol that were obtained by Arkhangel'skii *et al.* (22) in the PDMS polymer and multiplying the ratio by the estimated value for methanol obtained by Barrie (19), the latter being approximately 1.0×10^{-5} cm^2/sec.

Figure 3 shows the isotherm of the equilibrium amount of 1-propanol sorbed by the PDMS membrane. The isotherms for all alcohols exhibited linear behavior over the observed range of equilibrium relative pressures. These linear isotherms would be expected when sorption occurs at such low relative pressures that Henry's law is obeyed (23). Based on the diffusion coefficients that were obtained for various initial amounts of methanol, methanol should not have given a linear isotherm. However, it is possible that run-to-run variability obscured the presumed systematic deviation from linearity.

Table I. Diffusion Coefficients of Alcohols in a PDMS Membrane[a]

Amount of alcohol used (μL)	$D \times 10^5$ (cm^2/sec)			
	Methanol	Ethanol	1-Propanol	1-Butanol
5		0.61	0.58	0.26
10		0.56	0.55	0.36
15				0.36
20	1.04	0.65	0.53	
30	0.91	0.50	0.50	
40	0.97	0.64	0.59	
50	1.11	0.60	0.58	
60	0.65	0.64	0.57	
70	0.67	0.69	0.56	
80	0.68		0.52	
90	0.68		0.54	
100			0.50	
110			0.49	
120			0.56	

[a] Values were obtained by the sorption method and employed the long path gas cell.

Although the diffusion coefficient of a given compound can vary greatly from system to system, the diffusion coefficients for a series of similar compounds in a particular system should be related by the molecular volume. The Stokes–Einstein equation predicts that the diffusion coefficient is inversely proportional to the molecular radius of the diffusant. Assuming that the molecules are spheres, the molecular radii can be estimated from the molecular volumes according to the following equations:

$$\left(\frac{4\pi r^3}{3}\right) = V_m = \left(\frac{MW}{\rho N}\right) \tag{5}$$

$$r = \left(\frac{3}{4\pi N} \cdot \frac{MW}{\rho}\right)^{1/3} \tag{6}$$

where r is the molecular radius, V_m is the molecular volume, MW is the molecular weight, ρ is the density, and N is Avogadro's number. Since ethanol, 1-propanol, and 1-butanol should have been present as monomers in the PDMS slab, the value of D_0 for methanol that was thought to be representative of the monomeric state was used in the construction of a plot of D_0 versus the estimated molecular radius of each alcohol (Fig. 4). A linear relationship is obtained

Table II. Comparison of D_0 Values for Various Alcohols in PDMS

	$D_0 \times 10^5$ (cm^2/sec)				
	This study (mean ± SD)[a]	Barrie (19)[b]	Radovanovic *et al.* (20)[c]	Okamoto *et al.* (21)[d]	Arkhangel'skii *et al.* (22)[e]
Methanol	1.01 ± 0.09	1.0			2.50
Ethanol	0.61 ± 0.06		0.60	0.45	1.45
1-Propanol	0.54 ± 0.03				1.00
1-Butanol	0.33 ± 0.06				0.63

[a] At 21 ± 1°C.
[b] At 30°C.
[c] At 30 ± 1°C.
[d] At 25°C.
[e] At 35°C.

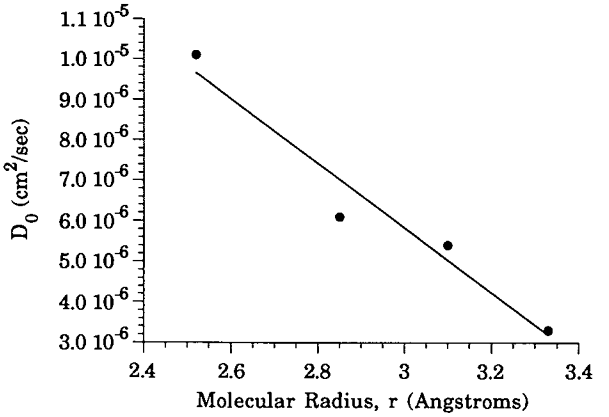

Fig. 4. Plot of the diffusion coefficient, D_0, versus the estimated molecular radius for the four alcohols employed in the sorption study. The correlation coefficient for the linear fit is 0.976.

with a correlation coefficient of 0.976. If the average of the diffusion coefficients for the four highest methanol concentrations had been used instead, the correlation coefficient for the linear regression of D_0 versus the molecular radius would have been only 0.916. This comparison supports the proposal that dimer formation occurred with the higher initial concentrations of methanol. More importantly, Fig. 4 indicates that the results obtained using this new method adhere to established theory.

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