Oxygen Permeation Through FEP Teflon and Kapton Polyimide

SUMMARY

The presence of oxygen in a gas sample causes a significantly different flame ionization detector (FID) response to hydrocarbons from that obtained for oxygen-free samples.[1] Use of a polymeric membrane between the sampling source and the FID detector provides a convenient means to reduce oxygen concentration in the permeant gases to sufficiently low levels to prevent interference with the normal FID response. Whereas Teflon polymers are useful for such membrane applications up to 200°C, Kapton polyimide is thermally stable up to at least 250°C; however, no known measurements of transport properties for O_2 in this material have been reported to date. As part of a program to study and minimize this so-called "oxygen effect" the permeability and diffusivity of oxygen in FEP Teflon and in Kapton were measured for oxygen partial pressures ranging from 3.2 to 22 cm (Hg). Measurement temperatures ranged from 40 to 85°C for FEP Teflon and from 171 to 252°C for the Kapton. Fick's law with a constant diffusivity describes the oxygen diffusion process, and Henry's Law describes sorption over the range of temperatures and low oxygen partial pressures studied. Arrhenius expressions with constant activation energies provide satisfactory descriptions of the temperature dependence of diffusivity and permeability data in both polymers. Constant van't Hoff sorption enthalpies are, therefore, also observed. The values of these enthalpies are in the range from −2 to −3 kcal/mol for both polymers.

EXPERIMENTAL

Materials. The polymers used in this study were commercial film samples. The 2- and 5-mil FEP (type A) films were kindly supplied by the Livingston Coating Corporation of Charlotte, NC. The 2-mil Kapton films were kindly supplied by the E. I. DuPont Company, Circleville, OH. All

TABLE I
Diffusion Coefficients for Oxygen in FEP Teflon and Kapton Polyimide

Polymer	Temperature (°C)	$D \times 10^7$ (cm^2/sec)
5-mil		
FEP Teflon	36.8	2.83
	46.0	3.388
		3.421
		3.92
	68.0	9.47
	75.0	15.2
	98.8	23.0
2-mil		
Kapton	137.3	0.963
		1.038
	160.0	1.683
		1.353
	165.8	1.168
		2.086
	200.8	4.287
		4.19
	216.6	3.206
	237.2	5.976
		5.938

Journal of Applied Polymer Science, Vol. 26, 2805–2809 (1981)

© 1981 John Wiley & Sons, Inc.

CCC 0021-8995/81/082805-05$01.00

TABLE II
Permeabilities of Oxygen in FEP Teflon and Kapton

Polymer	Temperature (°C)	Permeability × 10^{10} [cm^3(STP) cm/ cm^2 cm Hg s]
5-mil		
FEP Teflon	84.9	30.05
	74.9	19.76
	44.7	8.31
2-mil		
FEP Teflon	59.8	17.40
	40.0	9.067
2-mil		
Kapton	251.6	5.427
	231.8	5.001
	211.2	3.683
	189.0	3.176
	170.6	2.550

helium carrier and sweep gases were obtained from Air Products, Inc., Tamaqua, PA with less than 1 ppm O_2 impurity. The 500-ppm O_2 in helium used in the calibration of the gas chromatograph (GC) and the various O_2/helium mixtures used in the membrane transport work were obtained from Airco, Inc., Montvale, NJ.

Equipment and Procedures. A continuous permeation cell, described by Yi-Yan et al.,[2] was used in the present work with a Shimadzu 6AM gas chromatograph equipped with a 1.5-m MS-5A molecular sieve column and a high-sensitivity thermal conductivity detector (TCD). Calibration of the gas chromatograph was performed using a standard 500-ppm oxygen-in-helium stream diluted to different concentrations by mixing with a pure helium stream using a precision gas proportioner. A Shimadzu C-RIA electronic integrator was used to measure peak areas.

The oxygen stream used on the upstream side of the membrane during permeation runs was formulated by diluting known cylinder concentrations of O_2 in helium with pure helium using a precision gas proportioner. A high flow rate of pure helium sweep gas was used to sweep the O_2 penetrant

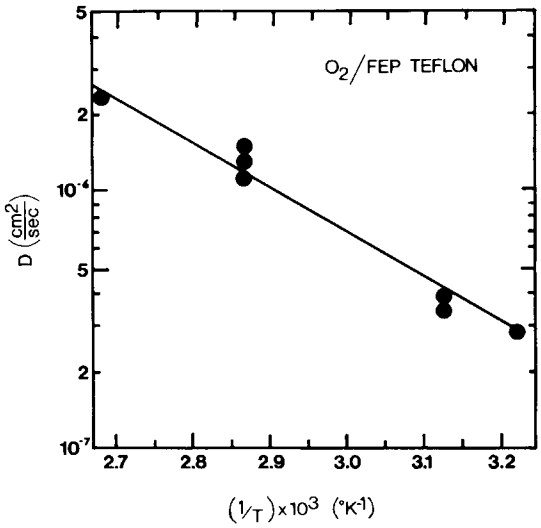

Fig. 1. Arrhenius plot of diffusion coefficients for oxygen in FEP Teflon between 36.8 and 98.8°C. The activation energy for diffusion determined from these data is 8.2 kcal/g mol.

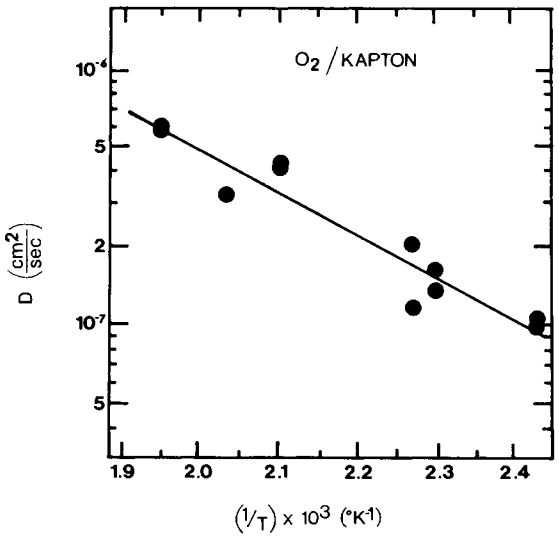

Fig. 2. Arrhenius plot of diffusion coefficients for oxygen in Kapton between 137.3 and 237.2°C. The activation energy for diffusion determined from these data is 7.4 kcal/g mol.

from the downstream membrane face and to maintain an effectively zero oxygen concentration at that point. The downstream helium sweep gas could be either routed periodically to a 10-cm^3 sample loop for batch analysis of O_2 concentration or sent directly to the TCD if continuous monitoring was to be performed.

The permeability P of the membrane to oxygen was calculated directly from the measured steady-state oxygen flux F using the expression

$$P = lF/p \tag{1}$$

where l is the membrane thickness and p is the upstream oxygen partial pressure.

The diffusivity of oxygen in each membrane was determined using the "method of moments" for

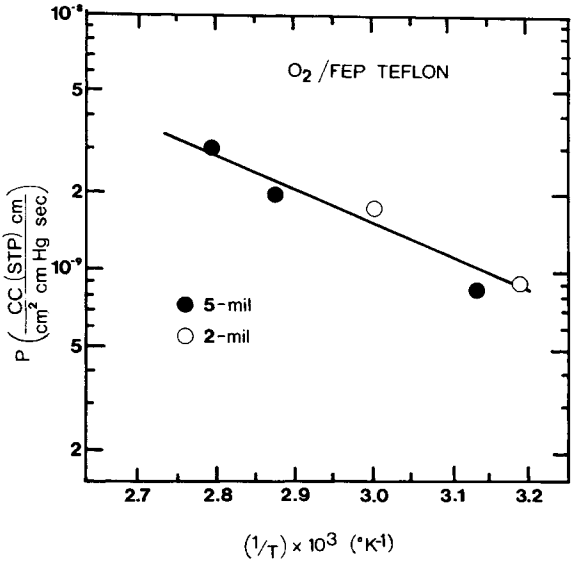

Fig. 3. Arrhenius-type plot of permeability coefficients for oxygen in FEP Teflon between 40 and 84.9°C. The apparent activation energy for permeation determined from these data is 6.1 kcal/g mol.

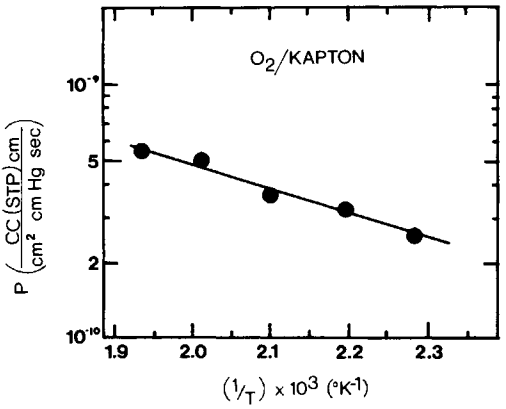

Fig. 4. Arrhenius-type plot of permeability coefficients for oxygen in Kapton between 170.6 and 251.6°C. The apparent activation energy for permeation determined from these data is 4.44 kcal/g mol.

analysis of transient permeation systems.[3] The method involves the integration of the ratio of the measured transient permeation rate, $\phi(t)$ (mol/s), to the asymptotic steady-state permeation rate ϕ_s, in the form

$$D = \tfrac{1}{6}l \Big/ \int_0 \left(1 - \frac{\phi(t)}{\phi_s}\right) dt \tag{2}$$

where l is, as before, the membrane thickness. Correct accounting for delay times due to nonzero residence times in gas lines permits determination of diffusion coefficients by this method with accuracies comparable to that of the classical time-lag experiment.[4]

RESULTS AND DISCUSSION

The diffusivities and permeabilities of oxygen in FEP Teflon and in Kapton are presented in Tables I and II for a variety of temperatures. All permeabilities and diffusivities were constant, within experimental error, for each polymer at a fixed temperature. Arrhenius plots of the diffusivities and permeabilities for O_2 in FEP Teflon and Kapton are shown in Figs. 1–4. The activation energies determined from these plots for FEP Teflon are in excellent agreement with reported values, as shown by the data in Table III. No data for oxygen diffusivity and permeability in Kapton are known to exist for comparison with the values obtained in the current study. It is clear, however, that both the oxygen diffusivity and permeability of Kapton are more than an order of magnitude lower than the values for FEP Teflon in the same temperature range (determined by extrapolating both sets of data to a common temperature for both polymers).

The well-known relationship between solubility, diffusivity, and permeability is represented by

TABLE III
Apparent Activation Energies for Oxygen Diffusion and Permeation in Teflon FEP and Kapton

Polymer	Activation energy for diffusion (kcal/g mol) (this study)	Activation energy for diffusion (kcal/g mol) (previous study)	Apparent activation energy for permeation (kcal/g mol) (this study)	Apparent activation energy for permeation (kcal/g mol) (previous studies)
FEP				
Teflon	8.2	8.3[a]	6.1	5.7[b]–6.1[a]
Kapton	7.4	···	4.4	···

[a] Reference 5.
[b] Reference 6.

eq. (3):

$$P = DS \tag{3}$$

where S is the Bunsen solubility coefficient for the gas in the polymer.[7] Since the temperature dependences of both the permeability and diffusivity for oxygen in the two polymers can be described by Arrhenius expressions with constant activation energies, the van't Hoff sorption enthalpy evaluated as the difference between the apparent activation energies for permeation and for diffusion is constant. The enthalpy of sorption for oxygen in FEP between 40 and 85°C is −2.07 kcal/mol, and that in Kapton between 177 and 252°C is −2.92 kcal/mol. A value of −2.2 kcal/mol has been reported for the enthalpy of sorption of oxygen in FEP Teflon at 25°C.[5] The usual magnitude of the enthalpy of sorption for oxygen in polymers ranges from +1 to −1 kcal/mol; however, values as low as −3.1 kcal/mol have been observed in glassy polycarbonate and poly(ethylene terephthalate).[6] The reported glass transition temperature of Kapton is near 300°C, while the value for FEP is dependent on copolymer formulation and is difficult to define. The sorption enthalpy results from the present study suggest that both polymers were below their respective glass transitions under the conditions of measurement.

The authors gratefully acknowledge support of this work under EPA Grant No. R805194010. Thanks are also extended to Nelly Yi-Yan for experimental assistance.

References

1. F. M. Black and L. E. High, *J. Environ. Sci. Health*, **A11,** 311 (1976).
2. N. Yi-Yan, R. M. Felder, and W. J. Koros, *J. Appl. Polym. Sci.*, **25,** 1755 (1980).
3. R. M. Felder, R. D. Spence, and J. K. Ferrell, *J. Polym. Sci.*, **19,** 3193 (1975).
4. R. M. Felder, *J. Membr. Sci.*, **3,** 15 (1978).
5. H. Yasuda and V. Stannett, in *Polymer Handbook*, 2nd ed., J. Brandrup and E. Immergut, Eds., Wiley-Interscience, New York, 1975.
6. H. Bixler and O. Sweeting, in *The Science and Technology of Polymer Films*, O. Sweeting, Ed., Wiley, New York, 1971.
7. V. Stannett, in *Diffusion in Polymers*, J. Crank and G. Park, Eds., Academic, New York, 1968.

W. J. KOROS
J. WANG*
R. M. FELDER

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27650

Received September 25, 1980
Accepted April 6, 1981

* Current address: Singer, Inc., 11800 Tech Rd., Silver Spring, Maryland 20904.