Determination of the Diffusivity in Elastomer Solutions by Batch Sorption Studies from a Dilute Liquid Phase

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ABSTRACT: A simple batch sorption method is examined for diffusivity determinations of binary solutions of low molecular weight organic compounds in amorphous polymers. The method is based on solute uptake from a stirred liquid solution by a polymer sheet sample submerged in the liquid solution and measurement of the liquid-phase concentration as a function of time. A transport model is discussed for the transient process of mass transfer between the stirred solution and the polymer phase, accounting for swelling of the polymer sheet and for concentration dependence of the diffusivity. The diffusion coefficient is evaluated by curve fitting of the results of numerical solution of the model equations to experimental data. Experimental toluene diffusivity data for the elastomers EPDM and PDMS are presented, as determined by the batch sorption method using an aqueous solution as the liquid phase. Good agreement between the experimental data and the calculated sorption curves is observed. A key parameter of a free-volume theory for diffusion in amorphous polymer was determined, by which the binary diffusion coefficient can be determined as a function of the composition and temperature, for a variety of diffusing solute compounds in the two elastomers examined. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66**: 347–353, 1997

Key words: diffusion; polymer solutions; elastomers

INTRODUCTION

The diffusivity of small organic molecules in amorphous polymers is of great interest to polymer manufacturing, where monomer and solvent recovery from the polymer matrix often is required, and to some polymer applications, such as in membrane separations. A method is introduced for determination of the diffusivity for binary polymer solutions by simple batch sorption studies. The method involves measurement of the rate of concentration decrease for a solute of a well-stirred liquid solution, while the solute is being transferred to a polymer slab, submerged in the liquid phase. The method presented has advantages in a simple operation procedure and suitability for application of a variety of quantitative analysis techniques.

A model is compiled for the mass-transfer process of solute from the liquid solution to the polymer phase. Strong concentration dependence of the diffusivity is a characteristic property of polymer solutions, which must be accounted for in the model by incorporation of an expression to correlate the diffusion coefficient and the mixture composition. To this purpose, a free-volume molecular diffusion theory due to Vrentas et al.[1] was used for the present study. Toluene diffusivity data for polydimethylsiloxane (PDMS) and for ethylene–propylene–diene–methylene (EPDM), as obtained by the batch sorption method, are reported.

In this article, the mathematical description of the sorption process is given first, followed by a brief discussion of the free-volume molecular diffusion theory applied. The experimental procedure is discussed and the data analysis is performed for the sorption experiments carried out.
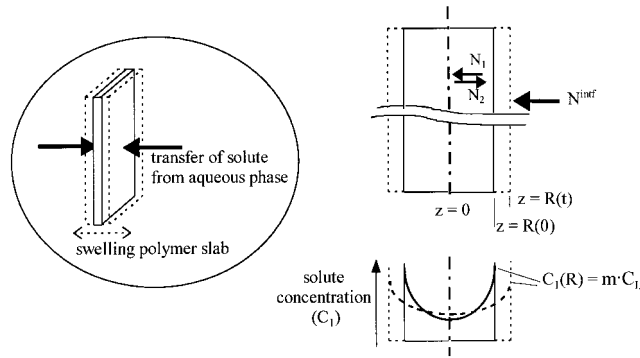
Figure 1 Schematic representation of the batch sorption mass transfer phenomena.

The results are discussed and, finally, conclusions are given.

MASS TRANSPORT MODEL

Figure 1 pictures the batch sorption process in a diagram. Mass transport is presumed only to take place in the direction perpendicular to the interface, formed by the two largest faces of the polymer slab, each having a constant surface area A. The polymer slab swells as a result of the penetration of solute. The position of the two faces of the slab is given by $z = \pm R(t)$.

For the polymer–solute mixture, which undergoes a relatively large change in composition, it is assumed that the specific volumes of the two components V_1 and V_2 (volume of component i/unit mass of component i) are independent of the composition, but may have different values. This means that there is no volume change on mixing of the polymer and the solute. Any influence of heat effects is neglected.

The differential equation describing the mass-transfer process in the polymer slab for any sorption experiment is given by

$$\frac{\partial C_{S,i}}{\partial t} = -\left(\frac{\partial}{\partial z} N_i\right) \tag{1}$$

where $C_{S,i}$ represents the amount per unit of volume of the mixture at a fixed position z and N_i is the flux of component i across a fixed plane. Here, weight based units are used. The mass flux N_i with respect to fixed coordinates is related to the diffusive flux J_i by[2]

$$N_i = C_i \cdot v^a + J_i^a \tag{2}$$

J_i^a represents the diffusive mass flux with respect

to a mixture having an average velocity v^a. The expression for the diffusive flux J_i^a depends on the choice of the reference (indicated by the superscript a) of the average velocity v^a. Because it is assumed that there is no volume change by mixing (V_1, V_2 = constant), the most convenient choice is the volume average velocity v^V, given by[3]

$$v^V = \sum_i (\phi_i \cdot v_i) = \sum_i (N_i \cdot V_i) \tag{3}$$

ϕ_i is the volume fraction of component i and v_i is the velocity of motion of component i with respect to fixed coordinates. For the sorption experiments, symmetry in the $z = 0$ face implies that fixed coordinates mathematically comply with $z = 0$.

For a binary system, the diffusive flux with respect to the volume average velocity is given by

$$J_i^V = -D \frac{\partial C_i}{\partial z} \tag{4}$$

Because mixing (by diffusion) gives no volume change, for $z < R$: $\sum N_i V_i = v^V = 0$ m/s. Hence, eqs. (1)–(4) combine to

$$z < R \rightarrow \frac{\partial C_{S,i}}{\partial t} = \frac{\partial}{\partial z}\left(D \frac{\partial C_{S,i}}{\partial z}\right) \tag{5}$$

Swelling of the polymer represents a complication. This effect needs to be accounted for since a polymer may swell as much as 200% in volume by solute uptake. The flux N_i^{intf} with respect to the interface is also found by combination of eqs. (1)–(4), using the volume average velocity with respect to the interface:

$$N_i^{\text{intf}} = C_i \sum_i (N_i^{\text{intf}} \cdot V_i) + J_i^V \tag{6}$$

N_i^{intf} represents the flux of component i with respect to the interface. There is no polymer flux through the interface, so $N_2^{\text{intf}} = 0$ and the flux for the solute across the interface is

$$N_1^{\text{intf}} = -\left(\frac{D}{1 - C_1 V_1}\frac{dC_{S,1}}{dz}\right)_{z=R} \qquad (7)$$

which follows directly from eq. (6). This flux is related directly to the depletion rate of the liquid phase by

$$-k_L \cdot 2A \cdot (C_L - C_L^{\text{intf}}) = 2A \cdot N_1^{\text{intf}} \qquad (8)$$

and

$$V_L \frac{dC_L}{dt} = 2A \cdot N_1^{\text{intf}} \qquad (9)$$

where the volume change of the liquid phase was neglected and C_L and V_L are the liquid-phase concentration and volume, respectively. Assuming a linear equilibrium isotherm at the interface yields

$$C_{S,z=R} = C_L^{\text{intf}} \cdot m \qquad (10)$$

where m represents the concentration distribution coefficient for the polymer and liquid phases.

Because $N_2^{\text{intf}} = 0$, the swelling rate is found from the volume flux across the interface, given by $N_1^{\text{intf}} \cdot V_1$:

$$\frac{dR}{dt} = -N_1^{\text{intf}} \cdot V_1 \qquad (11)$$

The boundary conditions are given by eqs. (12) and (13):

$$t = 0: C_L = C_L^0 \quad \text{and} \quad C_{S,-R<z<R} = C_S^0 \quad (12)$$

$$\left(\frac{dC_S}{dz}\right)_{z=0} = 0 \qquad (13)$$

Thus, the liquid-phase solute depletion curve for the sorption experiments performed is mathematically determined. The system of eqs. (5) and (7)–(11) can be solved numerically for the boundary conditions given by eqs. (12) and (13) if the diffusion coefficient is a known function of the solute concentration. A numerical integration scheme is given in the Appendix.

A FREE-VOLUME THEORY FOR DIFFUSION IN AMORPHOUS POLYMERS

The idea that diffusion in polymers is governed by continuous redistribution of "holes" in the polymer matrix, rather than by normal activation processes, has been well accepted since the late 1950s as a result of publications by Williams et al.,[4] Cohen and Turnbull,[5] Fujita,[6] and others. This presumed mechanism of free-volume fluctuations suggests diffusion models to be based on an expression for the probability of a solute molecule jump event, which is, in principle, dependent on the free-volume distribution, the size of the solute molecule, and some kind of activation energy term. Vrentas and Duda[1] presented one such theoretical model for the self-diffusion coefficient in a solute–polymer mixture. Their approach has been applied successfully to express the diffusion coefficient as a function of solute weight fraction and temperature for a variety of systems.[7]

The self-diffusion coefficient according to Vrentas and Duda[8,9] is given by

$$D_1 = D_{0_1}\exp\left(\frac{-E}{RT}\right)$$

$$\times \exp\left(\frac{-(w_1 V_1^* + w_2 \xi V_2^*)}{\left(\dfrac{K_{11}}{\gamma}\right)w_1(K_{12} - T_{g1} + T) + \left(\dfrac{K_{12}}{\gamma}\right)w_2(K_{22} - T_{g2} + T)}\right) \qquad (14)$$

The meaning of the parameters appearing in this equation is discussed briefly. Subscript 1 refers to the solute component, and subscript 2, to the polymer component. V_1^* and V_2^* represent the minimum hole specific volume (cm^3/g) required for a solute and polymer unit jump, respectively. w_1 and w_2 are the weight fractions in the mixture and ξ represents the ratio of the molar volume of a solute jumping unit to the molar volume of a polymer jumping unit, the volume of a jumping unit being the size of the cluster of solute molecules or monomer units making a diffusive jump. Furthermore, γ is an overlap factor; T_{g1} and T_{g2} are the glass transition temperatures; and K_{1i} and K_{2i} are free-volume parameters of component i; the first exponential term expresses the activation energy required for a diffusive jump of the solute. The relation between the self-diffusion coeffi-

Table I   Physical Substance Properties and Materials Specification

Variable	Units	Toluene	PDMS	EPDM
M	g/mol	92.13	74.1	70
$V*$	cm^3/g	0.917	0.905	1.005
$K_{11}/\gamma \cdot 10^3$	cm^3/g/K	1.45	0.932	0.814
$K_{21} - T_{g1}$	K	−86.32	−81	−157.3
$D_0 \cdot 10^{-4}$	cm^2/s	4.82		
$m_{SL} \cdot 10^{-2}$	[—]		2.0	3.1 (Keltan)
(Experimentally determined)				2.5 (Polysar)
χ	[—]		0.8	0.6

cient and Fick's binary mutual diffusion coefficient D is given by[10]

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \qquad (15)$$

where ϕ_1 represents the volume fraction of the solute ($\phi_1 = C_1V_1$), and χ, the Flory–Huggins interaction parameter.

Zielinski and Duda[11] suggested a number of methods to estimate the parameters of the model from other physical properties, such as pure component viscosity data. Table I lists the parameter values thus determined and used for the present study. Many experimental data indicate that the activation energy barriers for diffusion in polymers are negligible with respect to the free-volume effects, which implies application of $E = 0$ J/mol. Assuming that only single solute molecules engage in a diffusive jump, the parameter ξ is a mixture property, given by

$$\xi = \frac{M_1V_1^*}{V_{2j}} \qquad (16)$$

in which V_{2j} represents the molar volume of the polymer jump unit. Data available for reliable estimation of the ξ-parameter are limited, but ξ can be determined by model curve fits to experimental data.

EXPERIMENTAL

A 1 L solution of toluene in water was prepared by addition of a known weight of liquid toluene to a known weight of water, to obtain an approximately 100 mg/kg solution. The gas volume in the flasks containing the highly diluted solutions were kept small for the full duration of the experiments. A UV-vis spectrophotometer (Mitsubishi X-1100) equipped with a sample sipper device was used for concentration measurements (extinction at 254 nm wavelength). On introduction of the polymer sample in the flask, the experiment was started and the solution was stirred during the experiments using a magnetic stirring rod. The sample volume required for one concentration determination is small with respect to the total liquid volume of the flask. After conclusion of the diffusion experiment, the equilibrium concentration of the aqueous phase was measured after storage of the flask for a period corresponding to $Fo > 2$. (Fourier number $Fo = 4 \cdot D \cdot t/d^2$).

RESULTS

Toluene depletion curves for the aqueous phase in contact with elastomer sheets were determined experimentally for PDMS (cured Silopren LSR 2030, Bayer) and EPDM (uncured Keltan 514, DSM, and uncured Polysar 227, Bayer). By the method described in the previous sections, the depletion curve can also be calculated as a function of two unknown parameters: the free-volume parameter ξ and the mass transfer coefficient k_L for the stirred aqueous phase. By curve fitting of the calculated and experimentally determined curves, these two parameters can be evaluated. Table II gives the values for k_L and ξ, so deter-

Table II   Model Curve Fit Results

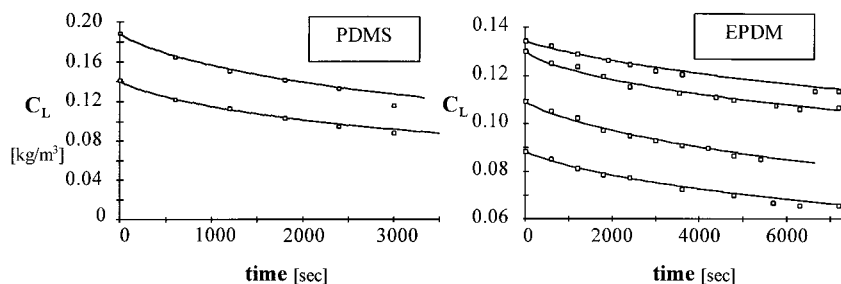|	ξ	$k_L \cdot 10^5$ [m/s]
EPDM Keltan	0.90	1.5
	0.93	2
EPDM Epsyn	0.88	2
	0.92	1.5
PDMS Silopren	1.42	5
	1.46	5

Figure 2 Experimental data and model curves for toluene sorption from an aqueous solution.

mined for a number of experiments. The resulting curves and the experimental data are shown in Figure 2.

The calculated curves match well with the experimental data. The level of scatter for the values of ξ as determined is acceptable. The difference of k_L for EPDM and PDMS is caused by the different conditions for the experiments. PDMS has a higher density than has water. The position of the sheets in the glass flasks was fixed during the experiments using a piece of steel wire. EPDM sheets, having a density smaller than water, were permitted to move freely with the stirred fluid.

Figure 3 shows the concentration dependence of the diffusion coefficient for toluene in the two polymers, respectively, based on the Vrentas and Duda free-volume theory according to the ξ-parameters evaluated experimentally. The curves are plotted for concentration ranges, representing the experimental conditions. It is seen that the binary diffusion coefficient of toluene/PDMS is almost concentration-independent, whereas for EPDM a 75% increase is observed. The curves resulting from extrapolation of the concentration range to 50 wt % are given in Figure 4, showing a maximum diffusivity for both curves. The difference of the solute weight fraction at which this maximum diffusivity appears in the curves is quite significant, which is caused by a combina-

tion of factors, i.e., free-volume differences for the two polymers and different values for the specific volume of a polymer jumping unit and for the Flory–Huggins interaction parameter.

The ξ-parameter, representing the ratio of the molar volumes of the solute and polymer jumping unit, is a property of the mixture. Application of the values $\xi_{EPDM} = 0.92$ and $\xi_{PDMS} = 1.44$ to eq. (16) yields an estimation for the molar volume of the polymer jumping unit V_{2j}. This parameter is a physical property of the polymer:

- EPDM: $V_j = 97$ cm^3/mol.
- PDMS: $V_j = 62$ cm^3/mol.

By eq. (16) and these values of V_j, for these two elastomers, the diffusivity can be predicted for various organic solutes, provided that the other parameters of the molecular diffusion model are known.

CONCLUSIONS

Experimental sorption curves are in good agreement with curves calculated on the basis of the following assumptions:
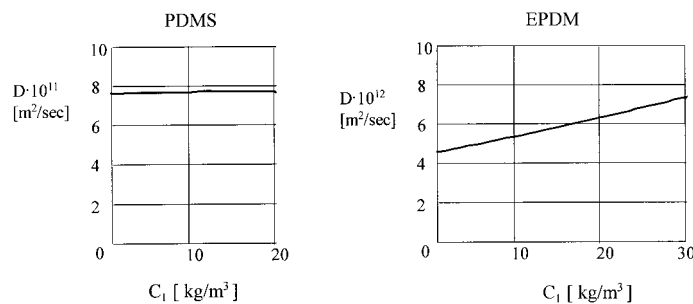

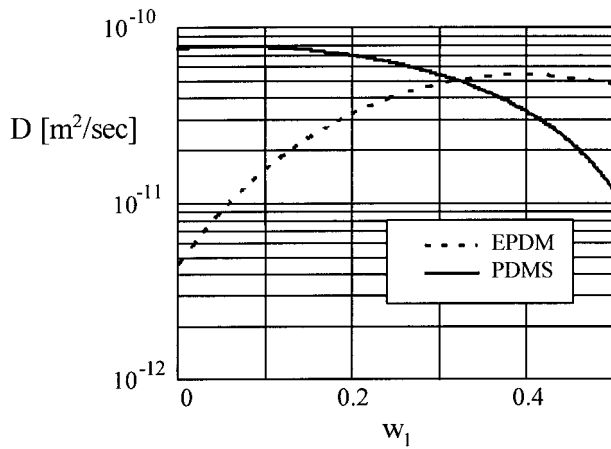**Figure 3** The diffusion coefficient as a function of toluene concentration in the polymer.

Figure 4 The diffusion coefficient as a function of toluene concentration for EPDM and PDMS determined by extrapolation.

- Homogeneous binary molecular diffusion according to a free-volume concept for the polymer phase.
- Swelling of the polymer solution with composition-independent specific volumes.
- Film theory for the liquid-phase equilibrium at the interface.

The agreement between experiment and theory indicates reliability of the transport model and experimental method applied for diffusivity determinations of elastomer solutions.

In dilute solutions of toluene in elastomers, the binary diffusion coefficient values determined are $D = 5 \cdot 10^{-12}$ m^2/s for EPDM, increasing approximately 100% as the toluene concentration increases from 0 to 5% by weight and $D = 8 \cdot 10^{-11}$ m^2/s for PDMS, showing little concentration dependence for toluene weight fractions less than 5%.

Evaluation of the molar volume of the polymer jumping unit V_j, a key parameter of a free-volume molecular diffusion theory due to Vrentas and Duda, by curve fitting yields $V_j = 97$ cm^3/mol for EPDM and $V_j = 62$ cm^3/mol for PDMS. By using these values for V_j, the application of the free-volume diffusion theory can be extended beyond the experimental conditions applied and to predict the diffusivity for solute compounds other than toluene.

NOTATION

Greek Symbols

χ Flory–Huggins interaction parameter [—]

ϕ_i volume fraction of component i [—]
γ overlap factor [—]
ξ molar volumes ratio of a solvent jumping and a polymer jumping unit [—]

Indices

Subscript

i, j property of component i or j
C property of the stirred liquid phase
S property of polymer phase

Superscript

intf   at phase interface
0   feed or initial value

Symbols

A	surface area of one slab face [m^2]
C	concentration [kg/m^3]
D	binary diffusion coefficient [m^2/s]
$D_{0,i}$	preexponential constant free-volume molecular diffusion theory [m^2/s]
D_i	self-diffusion coefficient of component i [m^2/s]
E	activation energy [J/mol]
J_i^a	diffusive mass flux with respect to a reference average velocity v^a [kg m^{-2} s^{-1}]
J_i	diffusive mass flux with respect to the volume average velocity [kg m^{-2} s^{-1}]
k_L	fluid side mass transfer coefficient [m/s]
K_{1i}, K_{2i}	free-volume parameters [m^3 kg^{-1} K^{-1}, K]
m	weight concentration based distribution coefficient [(kg/m^3)/(kg/m^3)]
M_i	molar weight of component i [kg/mol]
N_i	mass flux of component i with respect to fixed coordinates [kg m^{-2} s^{-1}]
R	(sheet thickness)/2 [m]
t	time [s]
T	temperature [K]
T_{g_i}	glass transition temperature of component i [K]
v^V	volume averaged velocity [m/s]
V_{2j}	molar volume of the polymer jumping unit [m^3/mol]
V_i	volume of component i per unit mass of component i [m^3/mol]
V_i^*	minimum hole specific volume required for a jump [m^3/kg]
V_L	liquid-phase volume [m^3]
w_i	weight fraction of component i [—]
z	sheet coordinate [m]

APPENDIX: NUMERICAL INTEGRATION SCHEME FOR THE BATCH SORPTION MASS TRANSFER MODEL

Notation

$$i = 1 \cdots n - 1; \, dz = i \cdot R/n$$

$$j = 1 \cdots m; \, t = j \cdot dt$$

$$D^i = [D(C_{S_{j,i}}) + D(C_{S_{j,i-1}})]^{/2}$$

Initialization

$$C_{L_0} = C_L^0, \, C_{S_{0,i}} = 0, \, C_{S_{0,n}} = 0, \, C_{S_{0,0}} = 0$$

[equivalent to eq. (12)]

$$R_1 = R^0, \, dz_1 = R^0/n$$

Transport Relations

$$\frac{C_{S_{j+1,i}} - C_{S_{j,i}}}{dt}$$

$$= \frac{D^{i+1}(C_{S_{j,i+1}} - C_{S_{j,1}}) - D^i(C_{S_{j,i}} - C_{S_{j,i-1}})}{dz_j^2}$$

[equivalent to eq. (5)]

$$C_{S_{j+1,0}} = C_{S_{j,0}} + D^1 \frac{2 \cdot dt}{dz_j^2} (C_{S_{j,1}} - C_{S_{j,0}})$$

[equivalent to eq. (13)]

$$C_{S_{j+1,n}} = \left(\frac{k_L}{m} + \frac{D^n}{(1 - C_{S_{j,n}} V_1) \cdot dz_j} \right)^{-1}$$

$$\times \left(k_L \cdot C_{Lj} - \frac{D^n}{(1 - C_{S_{j,n}} V_1) \cdot dz_j} C_{S_{j,n-1}} \right)$$

[equivalent to eqs. (7) and (8) combined]

$$C_{L_{j+1}} = C_{L_j} - \frac{2 \cdot A \cdot k_L \cdot dt}{V_L} \cdot \left(C_{L_j} - \frac{C_{S_{j,n}}}{m} \right)$$

$$- \frac{2 \cdot A \cdot dz_j}{V_L} (C_{S_{j+1,n}} - C_{S_{j,n}})$$

[equivalent to eq. (9) + correction]

$$R_{j+1} = R_j - \frac{V_L}{2A} \cdot (C_{L,j+1} - C_{L,j}) \cdot V_1$$

[equivalent to eq. (11)]

$$dz_{j+1} = R_{j+1}/n$$

$$C_{S_{j+1,i}} := \frac{R_j}{R_{j+1}} C_{S_{j+1,i}} + \frac{R_{j+1} - R_j}{R_{j+1}} C_{S_{j+1,i+1}}$$

In all expressions given above, C_L^{intf} was substituted by $C_L^{\text{intf}} = (C_{S,z=R}/m)$ according to eq. (10).

REFERENCES

1. J. S. Vrentas, J. L. Duda, and H. C. Hou, *J. Polym. Sci. Polym. Phys. Ed.,* **23,** 289 (1985).
2. R. Krishna and R. Taylor, *Multicomponent Mass Transfer,* Wiley, New York, 1994.
3. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* Wiley, New York, 1960.
4. M. L. Williams, R. F. Landell, and J. D. Ferry, *J. Am. Chem. Soc.,* **77,** 3791 (1955).
5. H. Cohen and D. Turnbull, *Chem. Phys.,* **31,** 1164 (1959).
6. H. Fujita, *Fortschr. Hochpolym.-Forsch.,* **3,** 1 (1961).
7. J. L. Duda, Y. C. Ni, and J. S. Vrentas, *J. Appl. Polym. Sci.,* **1,** 947 (1979).
8. J. S. Vrentas, *J. Polym. Sci. Polym. Phys. Ed.,* **15,** 417 (1977).
9. J. S. Vrentas, *J. Polym. Sci. Polym. Phys. Ed.,* **15,** 1715 (1977).
10. J. L. Duda, J. S. Vrentas, S. T. Ju, and H. T. Liu, *AIChE J.,* **28,** 279 (1982).
11. J. M. Zielinski and J. L. Duda, Predicting polymer/solvent diffusion coefficients using free-volume theory. *AIChE J.,* **38,** 405 (1992).