

# Free Volume Model and Diffusion of Organic Solvents in Natural Rubber

C. J. GUO,<sup>1\*</sup> D. DE KEE,<sup>2</sup> and B. HARRISON<sup>3</sup>

<sup>1</sup>Western Research Centre/CANMET, Devon, Alberta T0C 1E0, <sup>2</sup>Department of Chemical Engineering, University of Sherbrooke, Sherbrooke, Quebec J1K 2R1, and <sup>3</sup>Department of National Defence, DREO, Ottawa, Ontario K1A 0Z4, Canada

## SYNOPSIS

The concentration dependence of the diffusion coefficients and the equilibrium isotherms of benzene, *o*-xylene, ethylbenzene, and chloroform in natural rubber membranes at 303 K were experimentally determined. The data were used to critically test the predictive capability of the Vrentas–Duda free volume model. It was found that although the model works well for some polymer–solvent systems such as toluene–polystyrene, the use of some of the parameters from pure component properties yields unacceptably low diffusion rates for the rubber–solvent systems studied. The parameters  $D_{oi}$  and  $\xi$  obtained from experimental zero-concentration diffusivity data, and parameter  $\hat{V}_1^*$  calculated from the solvent molecular geometries are needed to achieve good predictions. The diffusion coefficients described by the revised model can be used to predict quite well the breakthrough times of the rubber–solvent systems that were also experimentally measured by a permeation method. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

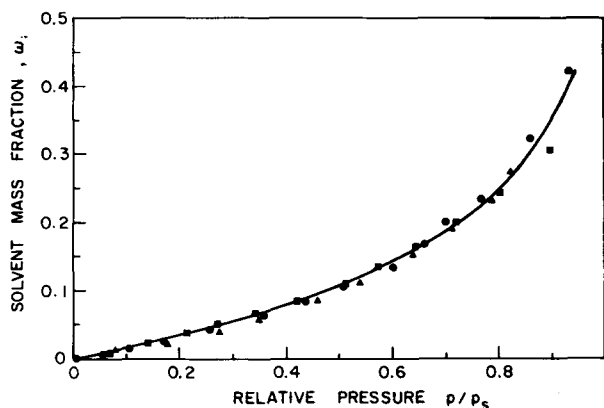
Knowledge of the experimental data and of the theoretical predictions of the diffusion rates of small solvent molecules in polymers are essential for many engineering applications where the molecular diffusion of the solvent is the rate-limiting step. For many years a reasonably simple model has been sought that can predict the diffusion coefficients and their concentration and temperature dependence for a polymer–solvent system from pure component data. Most recently, Zielinski and Duda<sup>1</sup> made such predictions for several polymer–solvent systems from the properties of the solvent and the polymer involved in the system. Model parameters for a number of organic solvents and polymers have been tabulated. It would represent significant progress if these parameters could be used to predict the diffusion coefficients for the systems tested (there would be a large number of systems considering the combination of all the solvents and polymers listed).

In this study, the sorption equilibrium and diffusion kinetic data for four organic solvents, benzene, ethylbenzene, *o*-xylene, and chloroform, in natural rubber membranes was experimentally determined. These data were used to test the free volume model for its predictive capability. We also used the model to predict the breakthrough times, and the predictions are compared with the experimental results measured by a permeation method.

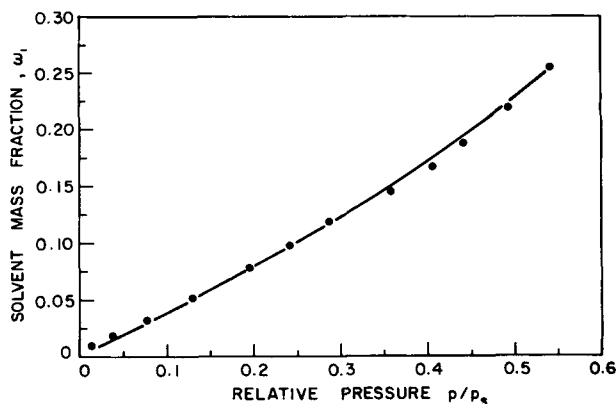
## EXPERIMENTAL

The experimental measurements were conducted using a Cahn 2000 electronic balance system. The details of this system have been described elsewhere.<sup>2</sup> The sorption uptake of the solvent vapor by the rubber membrane can be measured under the condition of constant temperature and constant vapor phase pressure with a measurable weight change of  $10^{-6}$  g. As the vapor phase pressure of the solvent is successively increased, the concentration dependence of the diffusion coefficients is obtained. For the same sorption systems, a permeation cell can be used to measure the time for a given solvent liquid

\* To whom correspondence should be addressed.



**Figure 1** Adsorption isotherms of benzene, ethylbenzene, and *o*-xylene in natural rubber at 303 K.



**Figure 2** Adsorption isotherms of chloroform in natural rubber at 303 K.

to permeate through the rubber membrane of a known thickness.<sup>3</sup> A microcomputer with a data acquisition program simultaneously records the experimental data from both tests. The organic solvents (purity > 99%) used in this study were purchased from the Aldrich Chemical Co. They were further purified by a freeze-thaw operation before introduced to the sorption system.

For the sorption uptake method, the diffusion coefficient of a solvent relative to the stationary rubber sample  $[(D_1)_2]$  was calculated by eq. (1) from the initial slope of the kinetic uptake curve ( $M_t/M_\infty$  vs.  $t^{1/2}$ ) of a solvent-rubber system:

$$(D_1)_2 = \frac{\pi l_a^2}{4} \left( \frac{\partial(M_t/M_\infty)}{\partial t^{1/2}} \right)^2 \quad (1)$$

where  $l_a$  is the half thickness of the original dry rubber film.

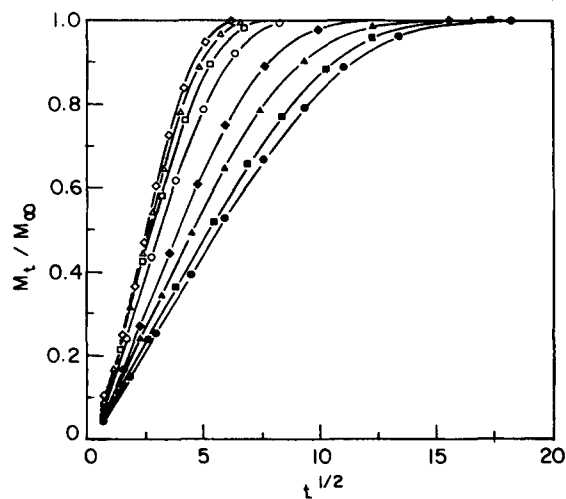
## RESULTS AND DISCUSSION

### Sorption Equilibrium and Concentration Dependence of Diffusion Coefficients

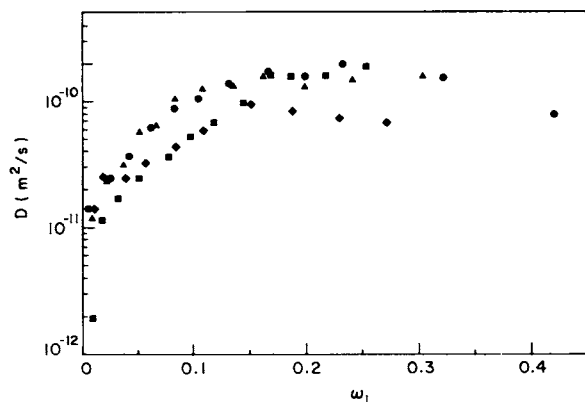
Figures 1 and 2 show the sorption isotherms of benzene, ethylbenzene, and *o*-xylene and for chloroform in natural rubber at 303 K, respectively. The symbols are the experimental points and the solid lines represent the Flory-Huggins model fitting to the data with interaction parameter  $\chi = 0.57$  for benzene, ethylbenzene, and *o*-xylene in natural rubber and  $\chi = 0.25$  for chloroform. The equilibrium results indicate that chloroform is a "better" solvent for natural rubber than benzene, ethylbenzene, or *o*-xylene. The three aromatic solvents have essentially the

same solubilities in the natural rubber at this temperature. The Flory-Huggins model provides a good description of the sorption equilibrium behavior of these rubber-solvent systems.

Figure 3 shows the kinetic uptake curves for benzene in natural rubber at 303 K, which typifies the results from the sorption measurements. As the solvent concentration increases, a slight curvature can be observed in the initial parts of the uptake curves that reflects the effect of the heat of adsorption. Its effect on the determination of diffusion coefficients is, however, not significant in this case. Using eq. (1), the diffusion coefficient of a solvent relative to the stationary rubber component  $[(D_1)_2]$  is obtained from the initial straight line parts of the uptake curves. With the mass fraction ( $\omega_1$ ) and volume fraction ( $\phi_1$ ) of the solvent in a rubber-solvent sys-



**Figure 3** Sorption kinetic curves of benzene-natural rubber system at different concentrations at 303 K.



**Figure 4** The concentration dependence of the mutual diffusion coefficients of benzene, ethylbenzene, *o*-xylene, and chloroform in natural rubber experimentally determined by the sorption method at 303 K.

tem calculated from the sorption equilibrium data, the mutual diffusion coefficients

$$(D = (D_1)_2 / (1 - \phi_1)^2)$$

and the self-diffusion coefficients

$$(D_1 = D / \{(1 - \phi_1)^2 (1 - 2\chi\phi_1)\})$$

were also determined.

Figure 4 illustrates the concentration dependence of the mutual diffusion coefficients of the four solvents in the natural rubber at 303 K.

### Testing and Revision of Free Volume Model

The free volume theories are based on the assumption that the free volume available in a solvent-polymer system is the major factor controlling the rate of molecular diffusion. Zero volume change of mixing of the components is also assumed. The free volume model introduced by Vrentas and Duda<sup>4,5</sup> was successful in correlating and, in some cases, predicting the concentration and temperature dependence of diffusion coefficients.<sup>1,6</sup> The current form of the free volume model can be written in the following form for the mutual diffusion coefficient (with the energy term neglected):

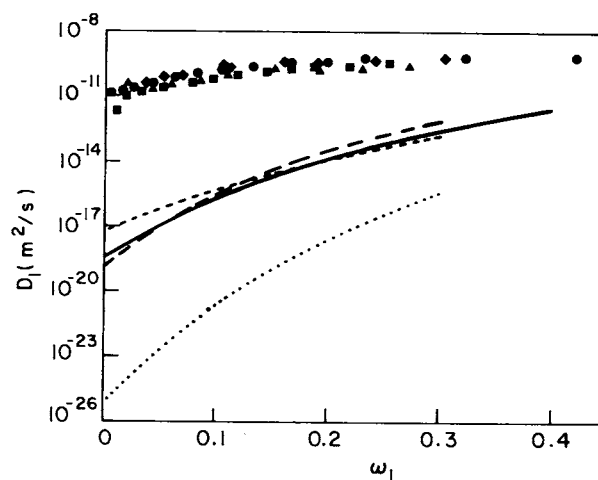
$$D = (1 - \phi_1)^2 (1 - 2\chi\phi_1) D_{o1} \times \exp \left\{ \frac{-(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\omega_1 \frac{K_{11}}{\gamma} (K_{21} - T_{g1} + T) + \omega_2 \frac{K_{12}}{\gamma} (K_{22} - T_{g2} + T)} \right\} \quad (2)$$

In Zielinski and Duda's recent work,<sup>1</sup> the model yields good predictions for the diffusion of some aromatic solvents in polystyrene. The model parameters for a number of solvents and polymers were summarized by the authors in two tables. With the experimental diffusion coefficients (Fig. 4) and the equilibrium data (Figs. 1, 2) measured for the four solvents in natural rubber in this study, a critical test of the model's predictability is made by comparing the predicted concentration dependence with the experimental results. Figure 5 shows the comparison of the experimental and predicted results. This prediction was made using the parameter values for the solvents and natural rubber listed by Zielinski and Duda.<sup>1</sup> It is evident that the predictions severely underestimate the diffusion coefficients for all the solvent-natural rubber systems studied.

In a recent study of the diffusion of rubber-solvent systems, Guo et al.<sup>7</sup> determined the parameters  $\xi$  and  $D_{o1}$  from the zero concentration diffusion data. These are quite different from those listed by Zielinski and Duda<sup>1</sup> as can be seen in Table I. Here,  $\xi_{\text{table}}$  and  $(D_{o1})_{\text{table}}$  are the parameter values given by Zielinski and Duda.<sup>1</sup>

Figure 6 indicates improved predictive capacity in the low concentration region when using experimentally determined values for  $\xi$  and  $D_{o1}$ . The prediction is still unacceptable in the high concentration region.

Guo et al.<sup>7</sup> show that the 0 K occupied volume of a liquid,  $V_1(0)$ , is not a universal representation of the critical volume requirement for solvent diffusion. For the diffusion of the solvents that jump in a single



**Figure 5** Comparison of the experimental and the predicted [eq. (2)] self-diffusion coefficients of benzene, ethylbenzene, *o*-xylene, and chloroform in natural rubber at 303 K.

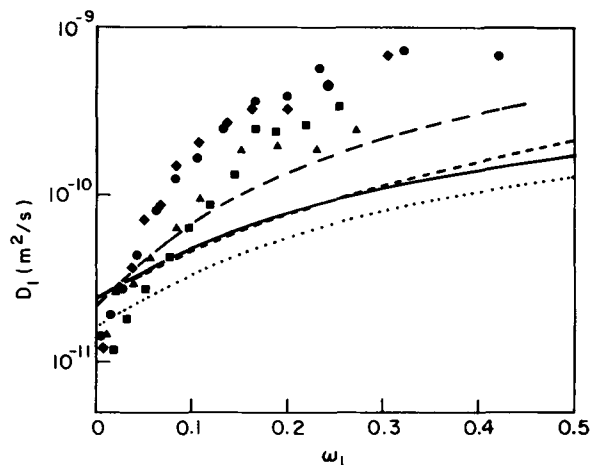
unit, an effective molecular diameter, calculated by eq. (3), was suggested:

$$d_{\text{eff}} = 0.6l_{\text{min}} + 0.3l_{\text{mid}} + 0.1l_{\text{max}} \quad (3)$$

where  $l_{\text{min}}$ ,  $l_{\text{mid}}$ , and  $l_{\text{max}}$  are the minimum, medium, and maximum dimensions of a molecule. An effective critical volume requirement for diffusion,  $V_{\text{eff}}$ , based on  $d_{\text{eff}}$ , correlated the diffusion data quite well. Therefore,  $V_{\text{eff}}$  calculated from the molecular geometries of the solvent molecules was used instead of  $\hat{V}_1^*$  in the free volume model. The predicted mutual diffusion coefficients are compared with the experimental data in Figure 7.

The results of Figures 5, 6, and 7 indicate the following.

1. The Vrentas–Duda free volume model provides a good mathematical form for the concentration and temperature dependence of the diffusion coefficients of the solvent–polymer systems.
2. Some of the suggested parameter values<sup>1</sup> such as  $\hat{V}_1^*$ ,  $\xi$ , and  $D_{o1}$  do not yield acceptable predictions of the diffusion coefficients because the replacement of  $\hat{V}_1^*$  by  $V_1(0)$  is not in general valid, especially for nonspherical molecules. The current methods to determine the value of parameter  $\xi$  from the physical properties of the components in the system are questionable. Recently Duda et al.<sup>8</sup> suggested estimating the polymer jumping unit (and therefore to determine  $\xi$ ) from the polymer relaxation measurement.
3. For small solvent molecules that can be assumed to jump as a single unit during a diffusive displacement, the effective critical volume for diffusion calculated from the molecular geometries resulted in satisfactory predictions of the diffusion coefficients and their concentration dependence.



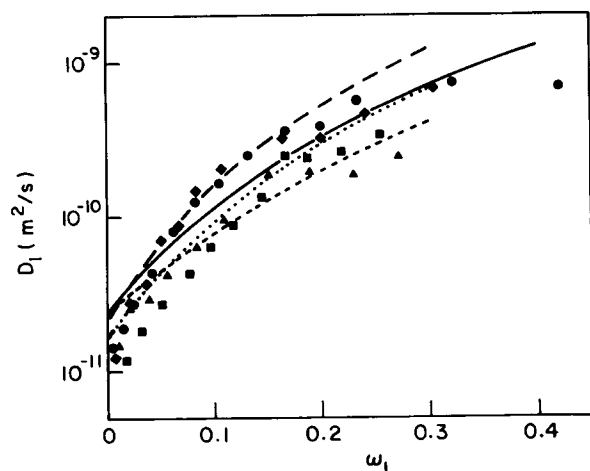
**Figure 6** Comparison of the experimental and the predicted [eq. (2)] self-diffusion coefficients of benzene, ethylbenzene, *o*-xylene, and chloroform in natural rubber at 303 K. The values of the model parameters  $\xi$  and  $D_{o1}$  were determined from the zero concentration diffusivities.<sup>7</sup>

### Predictions of Breakthrough Times for Solvent–Rubber System

The good agreement between the experimental and the predicted results in Figure 7 implies that a reasonable mathematical formulation of the concentration dependence of the mutual diffusion coefficient can be obtained. Using eq. (2) with the calculated  $V_{\text{eff}}$  substituting  $\hat{V}_1^*$ , along with the experimentally determined  $\xi$  and  $D_{o1}$ , a dimensionless diffusion equation with a concentration-dependent diffusivity can be numerically solved over the  $x$ -direction (thickness) to predict the time required for a given solvent to diffuse through a natural rubber membrane. The boundary conditions are that at the challenging surface of the rubber membrane ( $X = 0$ ), a saturated solvent liquid contacts the rubber at all times ( $C = c/c_o = 1$ ). At the outgoing surface of the rubber film ( $X = L$ ), zero solvent concentration was assumed. The calculated breakthrough time is defined to be the time when the dimensionless concentration  $C \geq 0.001$  at the outgoing surface of the membrane. Table II compares predicted results

**Table I** Parameters and  $D_{o1}$  from Zero Concn. Diffusion Data

	Benzene	Ethylbenzene	<i>o</i> -Xylene	Chloroform
$\xi_{\text{exp.}}$	0.472	0.499	0.524	0.458
$\xi_{\text{table}}$	2.007	2.865	3.176	1.737
$(D_{o1})_{\text{exp.}} \times 10^4 \text{ (cm}^2/\text{s)}$	1.222	1.58	1.653	1.019
$(D_{o1})_{\text{table}} \times 10^4 \text{ (cm}^2/\text{s)}$	11.3	4.61	12.39	5.49



**Figure 7** Comparison of the experimental and the predicted [eq. (2)] self-diffusion coefficients of benzene, ethylbenzene, *o*-xylene, and chloroform in natural rubber at 303 K. The parameter  $\hat{V}_1^*$  was replaced by  $V_{\text{eff}}$  calculated from the solvent molecular geometries.

with the experimental breakthrough times measured using a permeation cell. A fairly good agreement between the experimental and predicted times was obtained, considering that only the zero concentration diffusion coefficients<sup>2</sup> were used to determine the parameters  $\xi$  and  $D_{o1}$ .

## CONCLUSIONS

The mutual diffusion coefficients and sorption isotherms for benzene, ethylbenzene, *o*-xylene, and chloroform in natural rubber at 303 K were determined. Benzene and ethylbenzene show essentially the same values of diffusion coefficients in the natural rubber and the rate of diffusion of *o*-xylene in the same rubber is obviously lower. The solubilities of the three aromatic solvents in the natural rubber are quite similar. Chloroform is a better solvent than the aromatics for the natural rubber.

The use of an effective critical volume for diffusion and the values for parameters  $\xi$  and  $D_{o1}$  from zero solvent concentration diffusivities in the free volume model make it possible to predict the concentration dependence of the mutual diffusion coefficients and breakthrough times for the rubber-solvent systems. It can be concluded that although the current free volume model makes good predictions for the concentration and temperature dependence for some extensively studied polymer-solvent systems such as polystyrene-aromatics systems, it is still not possible to make such predictions for any polymer-solvent systems based on only pure component data. More work

is needed for the understanding and determination of parameters  $\xi$  and  $\hat{V}_1^*$ .

## NOMENCLATURE

$c$	Solvent concentration in a polymer-solvent system (gmol/m <sup>3</sup> )
$c_o$	Solvent concentration at the polymer-solvent interface of the ingoing side of the membrane in a permeation test (gmol/m <sup>3</sup> )
$D$	Mutual diffusion coefficient (m <sup>2</sup> /s)
$D_1$	Self-diffusion coefficient (m <sup>2</sup> /s)
$(D_1)_2$	Diffusion coefficient of the solvent relative to stationary polymer (m <sup>2</sup> /s)
$D_{o1}$	Preexponential factor in the free volume model (m <sup>2</sup> /s)
$d_{\text{eff}}$	Effective critical molecular diameter (m)
$K_{11}, K_{21}$	Free volume parameters for the solvent in the free volume model
$l_\alpha$	Half thickness of the polymer membrane (m)
$L$	Total thickness of the polymeric membrane in a permeation test (m)
$M_t, M_\infty$	Amount of solvent adsorbed in the membrane at time $t$ and at equilibrium, respectively (g)
$T$	Temperature (K)
$T_{gi}$	Glass-transition temperature of component $i$ (1 for solvent, 2 for polymer) (K)
$t$	time (s)
$\hat{V}_i^*$	Critical volume required for diffusive displacement of component $i$ (1 for solvent, 2 for polymer) (m <sup>3</sup> /g)
$V_{\text{eff}}$	Effective molecular volume calculated from $d_{\text{eff}}$ (m <sup>3</sup> /g)
$\omega_1$	Mass fraction of solvent in a polymer-solvent system

**Table II** Experimental and Predicted Breakthrough Times

Solvents	Breakthrough Times <sup>a</sup>	Predicted Breakthrough Times (min)
Benzene	9.0 (.69)	11.5
<i>o</i> -Xylene	26.0 (.73)	17.0
Ethylbenzene	12.5 (.68)	10.0
Chloroform	9.0 (.715)	10.0

Values are for the solvent liquids diffusing in natural rubber at 30°C.

<sup>a</sup> Measured by a permeation cell (film thickness in mm).

$\phi_1$	Volume fraction of solvent in a polymer-solvent system
$\chi$	Interaction parameter in the Flory-Huggins equation
$\xi$	Free volume model parameter taking into account the effect of solvent and polymer jumping unit volume
$\gamma$	Parameter taking into account the overlapping of free volume "owned" by different molecules

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