Estimation of Diffusion Coefficient for Solute–Polymer Systems

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SYNOPSIS

Diffusion coefficients are needed for the analysis of many mass transfer problems involving polymers. Since the diffusivity for such systems are strong functions of temperature and concentration, the analysis of these problems is greatly facilitated if predictive methods are available for the determination of the required diffusion coefficient. Because of the limitations of the theoretical approaches for estimating diffusivity, empirical correlation of solute–polymer diffusion coefficient data with physical properties of the solute were investigated. Chemical permeation measurements were made for several organic liquids through three elastomers (polychoroprene, butyl and nitrile rubber) at five different temperatures, ranging from 25 to 65°C. The collected diffusivities were correlated with liquid kinematic viscosity. Diffusivities (at different temperatures) depend mainly on the kinematic viscosity of solutes. The results also indicate a close relation between the variation of diffusivity and viscosity with temperature.

INTRODUCTION

Permeation of a chemical through a barrier is a three-step transport process involving (1) the sorption of molecules of the chemical at the contacted surface of the barrier, (2) the diffusion of the sorbed molecules through the barrier, and (3) the desorption of the molecules from the opposite surface of the barrier. Diffusion coefficients are needed for the analysis of many mass transfer problems involving polymers. Theoretical approaches to estimate diffusion coefficients are generally based on free volume theory.[1-6] In these models it is assumed that the mobility of penetrant molecules in a polymer matrix, as well as that of polymer segments, depends on the amount of free volume present in the system. More specifically, the rate of diffusion of a small molecule in a polymer depends primarily upon the ease with which polymer chains can exchange positions with the penetrant molecules. Such an exchange may require the cooperative movement of several polymer segments, which is made easier as the free volume of system is increased.

The various free volume theories differ in their definitions of free volume and in the assumptions that are made to calculate model parameters from properties of the solute and polymer. The properties needed to calculate the parameters are pure component viscosity and a small amount of self-diffusion data for a system consisting of trace of solute in the polymer.[3] These models have been used for glassy polymer–gas systems. Two of these models were investigated[7,8] for the solute–rubbery polymer systems. Comparisons of measured and predicted diffusion coefficients have shown the models to be only marginally accurate.

Because of the limitations of theoretical models for predicting diffusion coefficient for rubbery polymer–solute systems, empirical correlations were investigated. Southern and Thomas[9] studied the diffusion of various liquids in natural rubber, at 25°C, and concluded that the diffusion coefficient depends mainly on the liquid viscosity. Schwope and Reid[10] investigated the correlation of diffusion coefficient with properties representative of the solute size and shape. Their best correlations were with molecular weight.

In the first part of this work, the influence of temperature on the permeation properties of rubbery

polymers was investigated.[11] Measurements were made for the permeation of toluene and 1,1,1-tri-chloroethane through three polymers, namely, polychloroprene, butyl rubber (copolymers of iso-butylene with small amount of isoprene), and nitrile rubber (polymers of butadiene and acrylonitrile). Permeation and solubility tests were performed at five different temperatures, ranging from 25 to 65°C. The purpose of this paper is to perform additional permeation experiments and to examine the diffusion mechanism at non-steady-state and steady-state for a possible correlation that can predict diffusion coefficient. Measurements are made for the permeation of benzene through the same three elastomers at five temperatures. The experimental data from this work are combined with the data gathered from the previous work, and used for the theoretical study.

EXPERIMENTAL

The polymer materials, manufactures and nominal thicknesses are shown in Table I. Benzene (Reagent grade, Fisher Scientific, Norcross, GA) were used without additional purification. The apparatus used for the permeation experiment was the same one described in previous papers.[11-14] An ASTM permeation cell[15] (Pesce Laboratories, Kennett Square, PA) was used. The cell is constructed of two sections of straight glass pipe, each nominal sized to 51 mm (2 in.) diameter. The volume of the chamber design to hold the chemical is 45 mL, and the volume of the collecting medium chamber is 100 mL. For each experiment, a 3-in. square section was cut from the elastomer, and its thickness was measured with a thickness gauge (measurements to the nearest 0.001 in.). The material sample then was conditioned by placing it in a desiccator containing 42 wt % sulfuric acid for a minimum of 24 h. After removal from the desiccator, the sample was clamped in the middle of the cell, and the bolts holding the two chambers together were tightened to a torque of 30 in. lb with

Table I   Elastomers Tested

Material	Average Thickness (cm)	Supplier
Polychloroprene	0.053	Edmont (No. 29-870)
Butyl	0.051	NASA
Nitrile	0.058	Best (No. 22R)

a torque wrench. Nitrogen with a flow rate of 1000 mL/min was passed through the collecting chamber of the cell. After the chemical was charged to the challenge chamber of the cell, discrete samples (0.5 mL) of nitrogen were taken at 2 min intervals with a gas syringe. Analysis was obtained by a Perkin-Elmer Sigma 3B gas chromatograph with an Apezion column. Solubility of benzene in the polymers were determined by long-term immersion experiment. Samples of membranes were immersed in benzene for several days and the weight gains were measured.

RESULTS AND DISCUSSION

The permeation rate–time curves are shown in Figure 1 for benzene–polychloroprene pair. Similar curves were obtained for the other two polymers. As shown in Figure 1, the permeation rates at steady-state increased, and the permeation rate–time curves changed to a shorter time with increasing temperature.

The plots of logarithmic time required to reach the half-values of steady-state permeation rates for the benzene–polymer pairs against temperature are shown in Figure 2. Similar plots are prepared for toluene and 1,1,1-trichloroethane from the permeation data in Ref. 11, and are shown in Figures 3 and 4, respectively. As shown in these figures, the times ($t_{1/2}$) for all the pairs decreases with temperature. These curves are linear relationships. $t_{1/2}$ values are related to diffusion coefficients. If the diffusion coefficients are assumed to be independent of concentration, the following relation can be obtained from Fick's law[16]:

$$D = \frac{L^2}{(7.199t_{1/2})} \qquad (1)$$

where L is the thickness of membrane and D is the diffusion coefficient. Equation (1) along with Figures 2 through 4 can be used to calculate diffusion coefficient of solvent–polymer pairs as a function of temperature.

Semilog plots of steady-state permeation rates versus reciprocal of absolute temperature for benzene, along with the data from the previous work,[11] are shown in Figure 5. The apparent activation energy of permeation were calculated and ranged from 3 to 5 kcal/g mol for polychloroprene, 7 to 11 kcal/g mol for butyl, and 3-4 kcal/g mol for nitrile.

Semilog plots for solubility versus reciprocal of absolute temperature for benzene and the other two
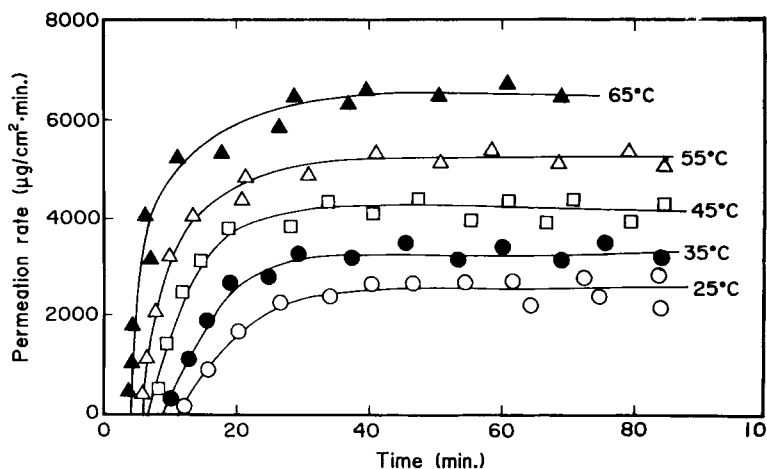
Figure 1   Permeation rate–time curves for the benezene–polychloroprene system.

chemicals[11] are shown in Figure 6. This figure shows how closely the experimental data obey the Arrhenius equation. From the slopes of the resulting straight lines the heat of solution of chemical/polymer pairs are calculated. The heat of solution for most of the pairs are less than 1 kcal/g mol.

From the data of the solubility and the steady-state permeation rates, the apparent diffusion coefficient ($\bar{D}$) are obtained by

$$\bar{D} = \frac{J \cdot L}{C_s} \qquad (2)$$

where J is the steady-state permeation rate and C_s is the solubility of chemical in polymer. Semilog plots of diffusion coefficient versus reciprocal of absolute temperature for the three chemicals are shown in Figure 7.

The magnitudes of diffusion coefficient of polymer–chemical pairs depend upon the properties of
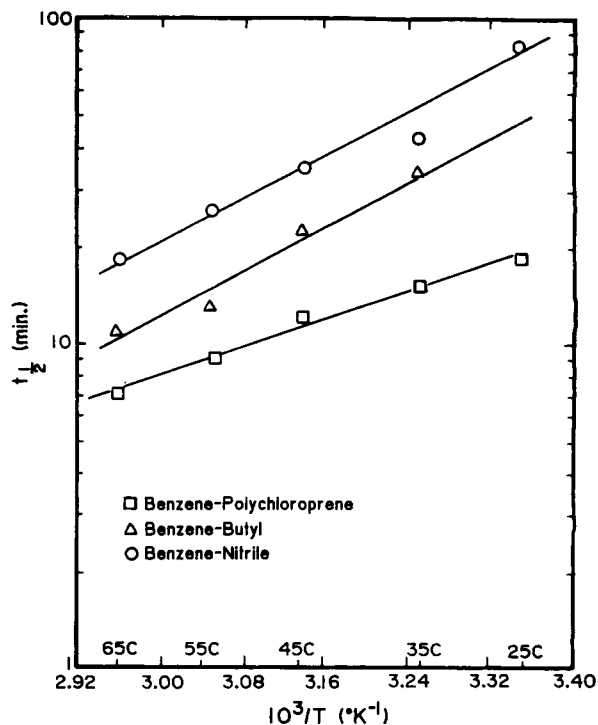

Figure 2   Time required to reach half-value of steady-state permeation rate for benzene.
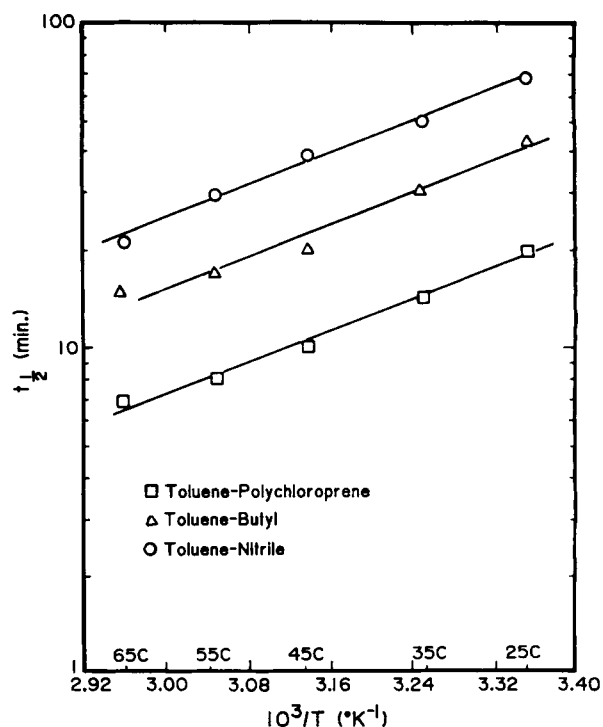

Figure 3   Time required to reach a half-value of steady-state permeation rates for toluene. (Data from Ref. 11.)
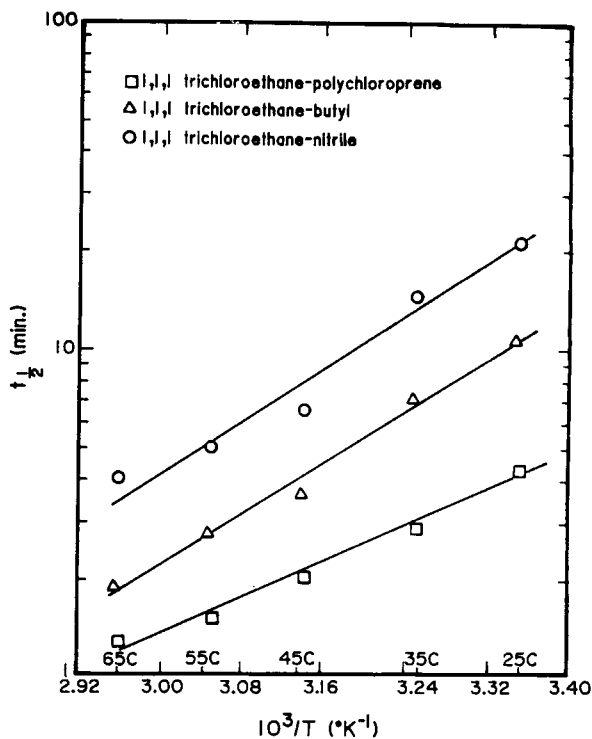
Figure 4 Time required to reach a half-value of steady state permeation rate for 1,1,1-trichloroethane. (Data from Ref. 11.)
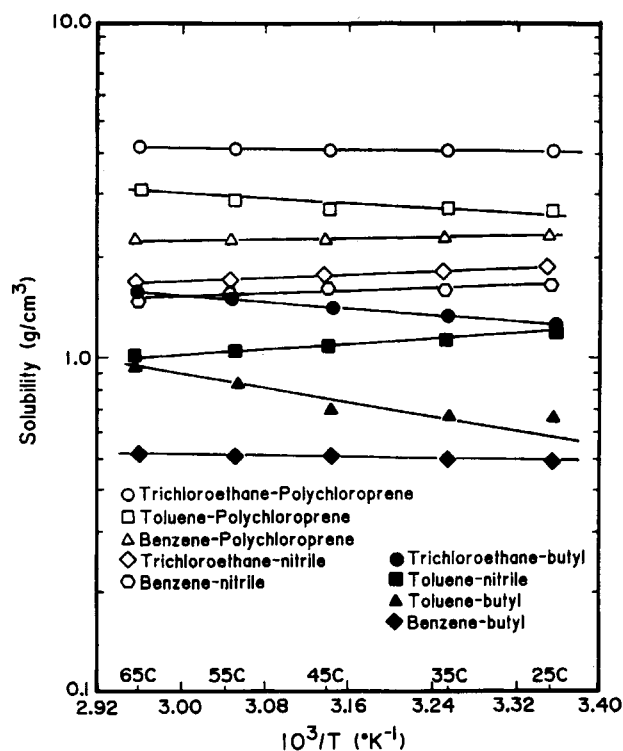

Figure 6 Arrhenius plots of solubility for the solute–polymer systems. (Data for toluene and 1,1,1-trichloroethane are from Ref. 11.)
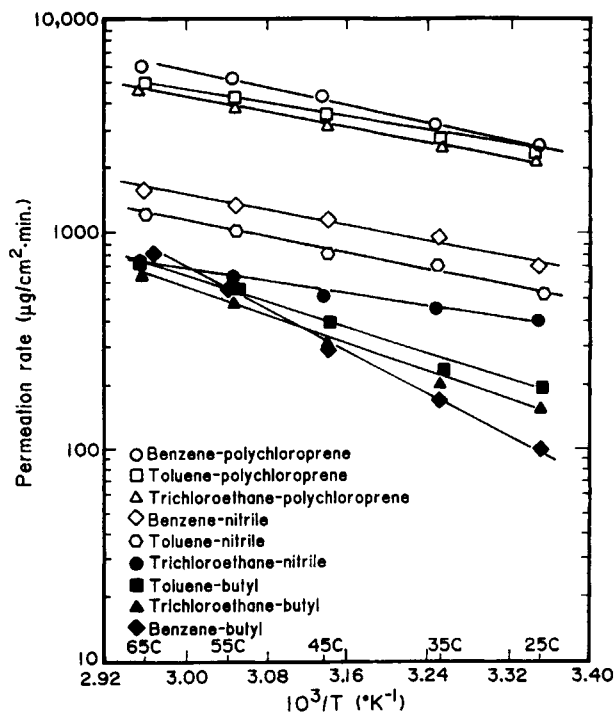

Figure 5 Arrhenius plots of flux for the solute–polymer systems. (Data for toluene and 1,1,1-trichloroethane are from Ref. 11.)

the membrane and the permeating species. An important property of the polymer might be the mobility of the polymer segments. The ease of rotation of the segments would determine the rate of passage of solutes of various sizes. The diffusion coefficient depends upon the size and shape of permeating species.

In recent years, there has been a spurt in research activity towards the use of free volume theories for the prediction of viscosity and diffusion coefficients. Paul[6] used Cohen–Turnbull diffusion theory to develop the following model for predicting solvent self-diffusion (D_1) in nonglassy polymer/solvent solutions:

$$D_1 = JD_{01}T^{1/2} \exp(-\gamma_1 \hat{V}_1^* / \hat{V}_F) \qquad (3)$$

where D_{01} = preexponential constant, T = absolute temperature, γ = numerical factor between $\frac{1}{2}$ and 1, $\hat{V}_1^*$ = critical volume required for diffusion of component 1 (solvent), $\hat{V}_F$ = specific free volume for mixture, and J = jump-back factor, usually between 5 and 11. Self-diffusion coefficient for pure solvent D_1^0 is related to viscosity by[16]
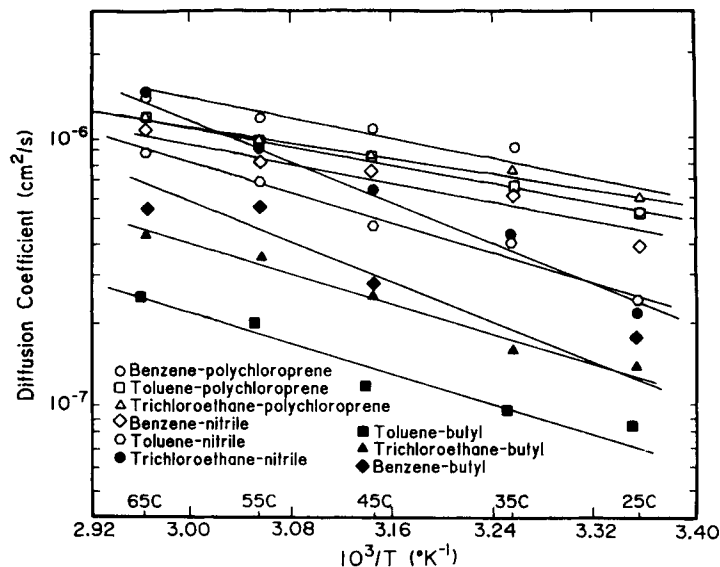
Figure 7 Arrhenius plots of diffusion coefficient for the solute–polymer system.

$$D_1^0 \mu_1 = (RT/V_1)(0.124 \times 10^{-16}\ \text{mol}^{2/3})V_{cl}^{2/3} \quad (4)$$

where $\hat{V}_1$ = molar volume at temperature T and V_{cl} = critical volume. For pure solvent, eq. (3) reduces to

$$D_1^0 = D_{01}T^{1/2}\exp(-\gamma_1\hat{V}_1^*/[\,\hat{V}_1 - \hat{V}_1(0\ \text{K})\,]) \quad (5)$$

Equations (3)–(5) can be combined to give the expression:

$$D_1 = \left(\frac{1}{\mu_1}\right)\frac{JRT(0.124 \times 10^{-16}\ \text{mol}^{2/3})V_{cl}^{2/3}}{V_1\exp(\gamma_1 V_1^*/[\,\hat{V}_1 - \hat{V}_1(0)\,])}$$

$$\times \exp\left(-\gamma_1\frac{\hat{V}_1^*}{\hat{V}_F}\right) \quad (6)$$

The relation between self-diffusion and mutual diffusion coefficient is[17]

$$D = \frac{D_1 X_2}{RT}\left(\frac{\delta\mu_1}{\delta\ln X_1}\right)_{T,P} \quad (7)$$

where X_1, X_2 = mole fractions of component 1 and 2, respectively, and μ_1 = chemical potential of the solvent. Substitution of eq. (6) in (7) yields

$$D = \left[\frac{J(0.124 \times 10^{-16}\ \text{mol}^{2/3})V_{cl}^{2/3}}{\mu_1 V_1\exp(\gamma_1 V_1^*/[\,\hat{V}_1 - \hat{V}_1(0)\,])}\right]$$

$$\times \left[X_2 - \frac{\delta\mu_1}{\delta\ln X_1}\exp\left(-\frac{\gamma_1\hat{V}_1^*}{\hat{V}_F}\right)\right] \quad (8)$$
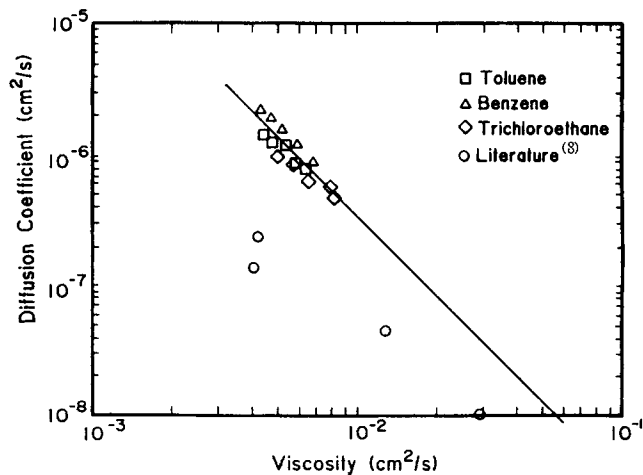

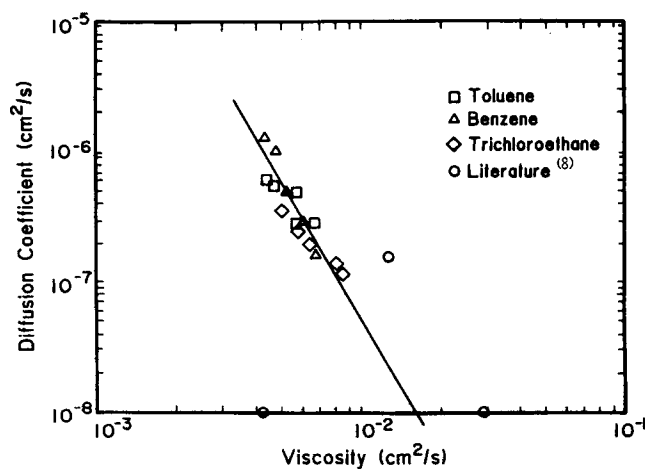**Figure 8** Correlation of diffusion coefficients with viscosity for polychloroprene.

Figure 9 Correlation of diffusion coefficients with viscosity for butyl rubber.
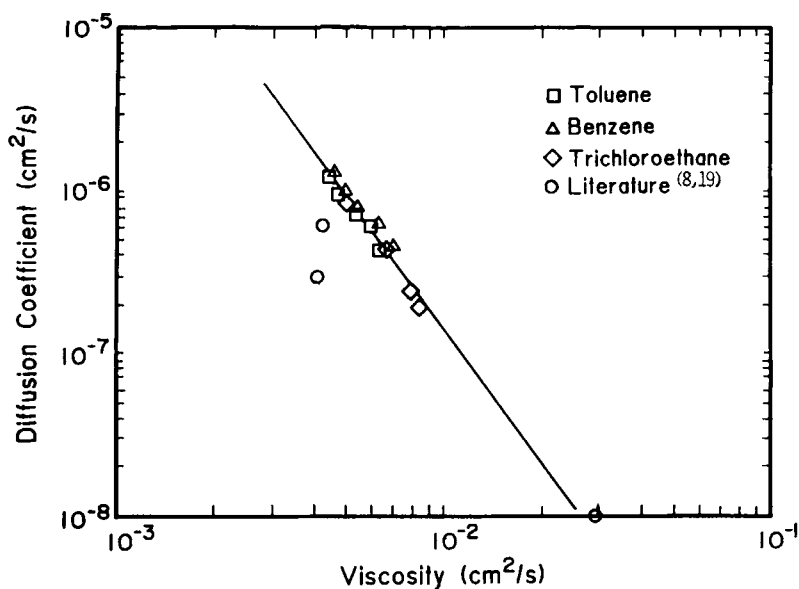
Figure 10   Correlation of diffusion coefficients with viscosity for nitrile rubber.

As explained by Paul,[6] V_1 is only a function viscosity and specific volume data for the pure solvent. Binary information on the polymer–solvent mixture is needed in order to evaluate the second bracket in eq. (8). Vrentas and Duda[17] explained the procedure for evaluating this expression based on the theory of Flory.[18] The procedure is complex and requires physical property data that are not generally available.

Equation (8) suggests that, for a given polymer, diffusion coefficient is mainly a function of viscosity and specific volume of pure solvent. Therefore, one expects a correlation between the diffusion coefficient and kinematic viscosity of solvent. The relation between diffusion coefficient and kinematic viscosity of pure liquids for the chemical–polymer pairs studied are shown in Figures 8–10. The data show a consistent trend with viscosity. The values of diffusion coefficient decreases linearly (on a log–log scale) with viscosity for each polymer studied.

In general, not many data on the diffusion coefficient of rubbery polymer–chemical systems are available in the literature. The published data for polychloroprene, butyl, and nitrile are shown in Figures 8–10.[19] The data show the same trend with viscosity, but they do not stay on the lines drawn through the experimental data gathered in this work. The reason is that all the published data are for the diffusion of chemicals through commercially available elastomers. These polymers which are manufactured by different companies are not exactly the same, due to the different plasticizers and fillers

used. Obviously the plasticizers have a direct effect on the diffusion coefficient of chemical/polymer systems.

CONCLUSION

Diffusion and permeation characteristics of rubbery polymers to pure solvents have been studied, and the effect of temperature on the diffusion coefficient of solvent–polymer pairs for the cases of non-steady-state and steady-state permeations was investigated. The time required to reach the half-value of steady-state permeation rates was shown to vary exponentially with reciprocal of absolute temperature for a given polymer. The diffusion coefficients are shown to be mainly a function of viscosity of the liquid. The values of diffusion coefficient decrease linearly (on a log–log scale) with viscosity for each polymer studied.

REFERENCES

1. H. Fujita, *Fortschr. Hochpolym-Forsch.*, **3**, 1 (1961).
2. J. S. Vrentas and J. L. Duda, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 403 (1977).
3. J. S. Vrentas and J. L. Duda, *J. AIChE*, **25**, 1 (1979).

4. J. L. Duda and J. S. Vrentas, *J. AIChE,* **28,** 272 (1982).
5. J. S. Vrentas, J. L. Duda, and A. C. Hou, *J. Polym. Sci. Polym. Phys. Ed.,* **23,** 2469 (1985).
6. C. W. Paul, *J. Polym. Sci. Polym. Phys. Ed.,* **21,** 425 (1983).
7. A. S. Bhown, E. F. Philpot, D. P. Segers, G. D. Sides, and R. B. Spafford, "Predicting the Effectiveness of Chemical Protective Clothing: Model and Test Method Development," EPA/600/S2-86/055, US Environmental Protection Agency, Cincinnati, OH, 1986.
8. R. Goydan, A. D. Schwope, and R. C. Reid, "Review of Models for Predicting Chemical Protective Clothing Effectiveness," Internal Report prepared on EPA Contract 68-03-3293, work assignment 0-01, EPA, Cincinnati, OH, 1986.
9. E. Southern and A. G. Thomas, *Trans. Faraday Soc.,* **63,** 1913 (1967).
10. A. D. Schwope and R. C. Reid, "Development and Assessment of Methods for Estimating Protective Clothing Performance," EPA/600/2-87/104, U.S. Environment Protection Agency, Cincinnati, OH, 1987.
11. N. Vahdat and M. Bush, *Chemical Protective Clothing Performance in Chemical Emergency Response,* ASTM STP 1037, J. L. Perkins and J. O. Stull, Eds., American Society for Testing and Materials, Philadelphia, 1989.
12. N. Vahdat, *Am. Ind. Hyg. Assoc. J.,* **48**(2), 155 (1987).
13. N. Vahdat, *Am. Ind. Hyg. Assoc. J.,* **48**(7), 646 (1987).
14. N. Vahdat and R. Delaney, *Am. Ind. Hyg. Assoc. J.,* **50**(3), 152 (1989).
15. N. W. Henry and C. N. Schlatter, *Am. Ind. Hyg. Assoc. J.,* **41,** 202 (1981).
16. K. D. Ziegel, H. K. Farensdorff, and D. E. Blair, *J. Polym. Sci. A-1,* **7,** 809–819 (1969).
17. J. S. Vrentas and J. L. Duda, *J. Polym. Sci. Polym. Phys. Ed.,* **15,** 417 (1977).
18. P. J. Flory, *Discuss. Farady Soc.,* **49,** 7 (1970).
19. G. C. Coletta, A. D. Schwope, I. Arons, J. King, and A. Sivak, *Development of Performance Criteria for Protective Clothing Used against Carcinogenic Liquids,* DHEW (NIOSH) Publication No. 79-106, Little, Cincinnati, OH, October 1978.