

Solvent Diffusion in Amorphous Polymers

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Synopsis

New diffusivity data are presented for solvent diffusion in poly(vinyl acetate), poly(methyl methacrylate), and polystyrene. These data are used to test the predictive and correlative capabilities of a recently proposed free-volume theory of diffusion. Comparisons of data and theory showed that the proposed theory provided an accurate description of diffusion in concentrated polymer solutions.

INTRODUCTION

Recent emphasis in the polymer industry on the removal of small amounts of volatile residuals for environmental and health reasons has initiated increased interest in the diffusion of solvents in molten polymers. Both diffusivity data for polymer-solvent systems above the glass transition temperature and a theory which has correlative and predictive capabilities are needed to facilitate the analysis and design of important processing steps. In this paper, we present new data for solvent diffusion in three amorphous polymers, poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), and polystyrene. In addition, some of these new diffusivity data are used to test the predictive and correlative capabilities of a recently proposed free-volume theory of diffusion.¹⁻⁶

THEORY

The new free-volume theory¹⁻⁶ appears to give the best available description of diffusion in concentrated polymer solutions at the present time. Although this theory describes the general behavior of the mutual diffusion coefficient for polymer-penetrant systems over wide ranges of temperature and concentration quite well, comparisons with experimental data^{3,5,7} show that the predicted values of the diffusivity are significantly higher than those determined from sorption experiments. Furthermore, use of the thermodynamic theory of Flory⁸ to determine the thermodynamic information needed to compute the diffusivity has limited the utilization of the proposed free-volume analysis. Although the theory of Flory satisfactorily describes the temperature and concentration dependences of the mixture specific volume and solvent chemical potential, the data needed to compute the parameters of this theory are frequently not available for polymer-solvent systems.

As a consequence of the above shortcomings, two modifications of the proposed free-volume theory have been recently introduced.⁹ First, to improve the predictive capabilities of the theory, one of the assumptions of the original version has been relaxed. It was previously assumed¹⁻⁶ that the temperature variation

of the diffusivity which results from the energy needed to overcome attractive forces could be ignored. It now appears that this assumption is the major source of error in the prediction of the mutual diffusion coefficient. Consequently, the theory has been revised to include a new parameter E , the energy per mole that a molecule needs to overcome attractive forces which hold it to its neighbors. A second modification of the new free-volume theory involves the introduction of a simplified thermodynamic model for the polymer-solvent system. This is done by introducing the following three assumptions:

1. All thermal expansion coefficients are approximated by average values in the temperature range under consideration.

2. The partial specific volumes of the polymer and solvent are considered to be independent of concentration.

3. The solvent chemical potential in the mixture can be satisfactorily approximated using the Flory-Huggins theory¹⁰ with a constant interaction parameter χ .

These three assumptions are not necessary but are introduced simply to facilitate utilization of the theory, with the presumption that they will lead to a small loss in accuracy.

With the above modifications, the free-volume equation for the mutual diffusion coefficient D can be written as

$$D = D_0 \exp\left(\frac{-E}{RT}\right) (1 - \phi_1)^2 (1 - 2\chi\phi_1) \exp\left[-\frac{(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}/\gamma}\right] \quad (1)$$

where

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma} \omega_1 (K_{21} + T - T_{g1}) + \frac{K_{12}}{\gamma} \omega_2 (K_{22} + T - T_{g2}) \quad (2)$$

$$\phi_1 = \frac{\omega_1 \hat{V}_1^0}{\omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_2^0} \quad (3)$$

Here, D_0 is a constant preexponential factor, ω_I is the mass fraction of component I , \hat{V}_I^* is the specific critical hole free volume of component I required for a jump, \hat{V}_I^0 is the specific volume of pure component I , and ϕ_I is the volume fraction of component I . Also, T_{gI} is the glass transition temperature of component I , K_{11} and K_{21} are free-volume parameters for the solvent, K_{12} and K_{22} are free-volume parameters for the polymer, γ is an overlap factor for free volume, and \hat{V}_{FH} is the average hole free volume per gram of mixture. Finally, ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. The definitions of the free-volume parameters K_{11}/γ , K_{21} , K_{12}/γ , and K_{22} , which are given elsewhere,^{3,4} are not needed in the present context. It should be noted that these four constants are directly related to the WLF constants of the solvent and polymer.^{3,6} The subscripts 1 and 2 refer to solvent and polymer, respectively.

The concentration and temperature variations of D can be determined for a particular polymer-solvent system from eqs. (1)–(3) if the following parameters are known: D_0 , E , χ , ξ , \hat{V}_1^* , \hat{V}_2^* , K_{11}/γ , K_{12}/γ , $K_{21} - T_{g1}$, $K_{22} - T_{g2}$, \hat{V}_1^0 , and \hat{V}_2^0 . These parameters of the theory can be evaluated if the following data are available:

1. Density-temperature data for the pure polymer and the pure solvent.
2. Viscosity-temperature data for the pure polymer and the pure solvent.

3. Three or more values of the polymer-solvent diffusivity at two or more temperatures.

4. Thermodynamic data, such as sorption equilibrium data, for the polymer-solvent system.

Procedures for determining the system parameters from the above data sets are described in detail elsewhere.⁹ Density data and correlations can be used to compute \hat{V}_1^* , \hat{V}_2^* , \hat{V}_1^0 , and \hat{V}_2^0 , and solvent and polymer viscosity data can be used to evaluate K_{11}/γ , K_{12}/γ , $K_{21} - T_{g1}$, and $K_{22} - T_{g2}$. The interaction parameter χ can be determined from available polymer-solvent thermodynamic data, and D_0 , E , and ξ can be computed using diffusivity data and a nonlinear regression analysis based on eqs. (1)–(3). Density, viscosity, and thermodynamic data are usually available for common polymer-solvent systems, and only a small amount of diffusivity data is required for the determination of D_0 , E , and ξ .

The correlative capabilities of the proposed theory can be tested by using all of the diffusivity data from a given data set to determine D_0 , E , and ξ and then noting how well the resulting theoretical curves agree with the experimental data. It was shown previously⁹ that the free-volume theory based on eqs. (1)–(3) provided good correlations of toluene-polystyrene and ethylbenzene-polystyrene diffusivity data over wide ranges of temperature and concentration. The predictive capabilities of the theory can be tested by using a small number of data points from a given set of diffusivity data to determine D_0 , E , and ξ and then comparing the theoretical predictions based on these parameters with all of the experimental data. The present theory produced good predictions of the mutual diffusion coefficients for the toluene-polystyrene and methyl acetate-poly(methyl acrylate) systems over wide temperature and concentration ranges.⁹ In this study, the correlative and predictive capabilities of the proposed theory are further tested using the new diffusivity data.

The free-volume analysis also predicts⁴ that the parameter $\gamma \hat{V}_2^* \xi / K_{12}$ is a linear function of the molar volume of a solvent jumping unit at 0°K. This prediction can be easily checked for solvents for which the entire molecule performs a jump since molar volumes at 0°K can be estimated using group contribution methods.¹¹⁻¹³ In a previous study,¹⁴ it was shown that experimental data were in agreement with this prediction for solvent diffusion in PVAc, polystyrene, poly(methyl acrylate), and poly(ethyl methacrylate). In this paper, we determine if PMMA diffusivity data are consistent with this free-volume result.

EXPERIMENT

Diffusivity data in this investigation were collected using a step-change sorption experiment. The PMMA and polystyrene data were obtained using a high-temperature quartz spring sorption balance, and the PVAc data were collected using an automated Cahn electrobalance system. The apparatus and experimental procedure are described in detail elsewhere.^{7,15-17} An average diffusivity was computed from the initial slope of the sorption curve plotted against the square root of time. It has been shown elsewhere¹⁸ that it is possible to equate this average diffusivity, with less than 5% error, to the actual diffusivity corresponding to a particular intermediate concentration in the concentration interval studied during the sorption experiment. This method is applicable even when there is a twentyfold change in the diffusion coefficient in the concentration interval covered in a particular sorption experiment.

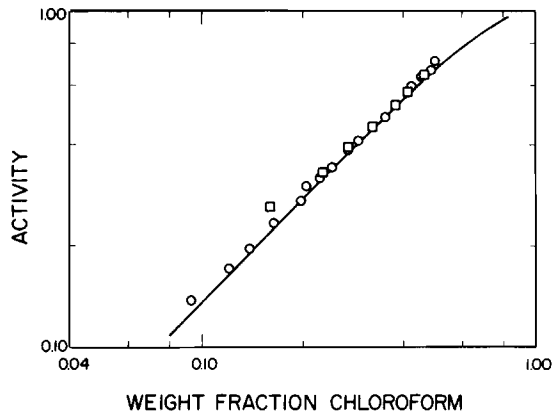


Fig. 1. Comparison of Flory-Huggins theory with thermodynamic data for PVAc-chloroform system. (○) 45°C; (□) 35°C. $\chi = -0.5$.

Experiments could be conducted on the quartz spring sorption balance at temperatures at least up to 180°C; no effort was expended in this investigation in determining the upper operating limit of this apparatus. Diffusivity data could be collected only up to 50°C on the Cahn electrobalance because of the temperature limitations of the electronic components of this apparatus. The upper limit of the solvent concentration was determined either by the pressure or temperature control limitations of the quartz spring sorption balance and the

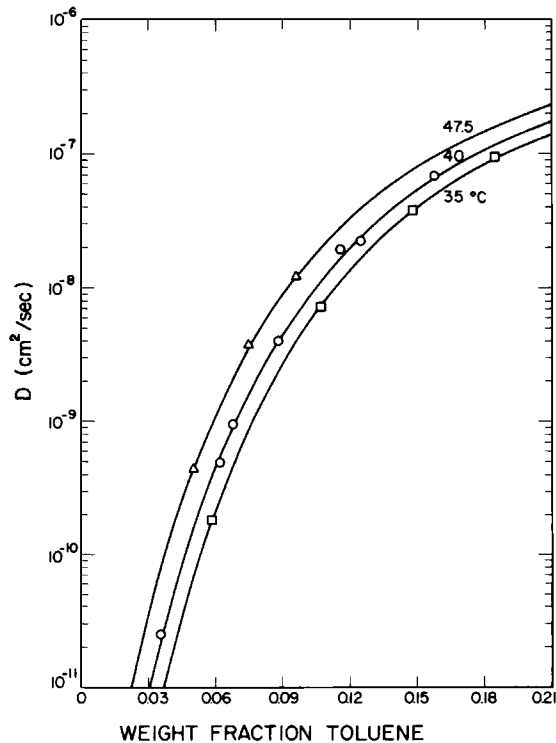


Fig. 2. Correlation of diffusivity data for the PVAc-toluene system using free-volume parameters contained in Table II. (Δ) 47.5°C; (○) 40°C; (□) 35°C.

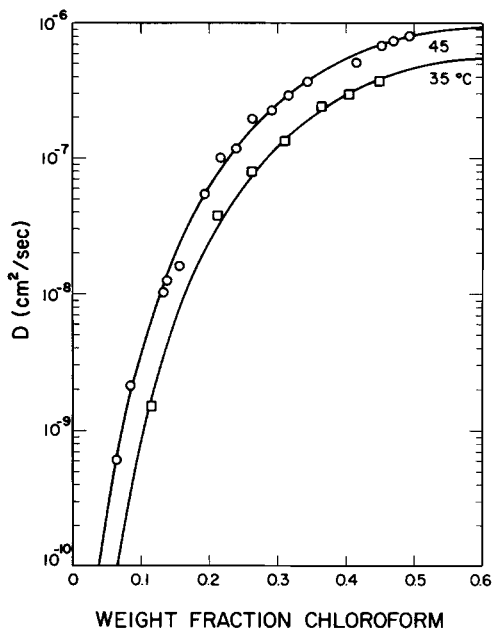


Fig. 3. Correlation of diffusivity data for the PVAc-chloroform system using free-volume parameters contained in Table II. (O) 45°C; (□) 35°C.

Cahn electrobalance. Both pieces of equipment were constructed to operate at penetrant vapor pressures no higher than atmospheric, and, in some cases, this limited the range of solvent concentrations which could be studied. For instances when the pure solvent limit was in principle possible, the maximum solvent concentration was determined by the temperature control characteristics of the equipment. Temperature control becomes difficult as the solvent feed temperature approaches the temperature of the polymer sample.

The polymers used in this study were commercial samples with the following weight-average molecular weights: polystyrene (275,000), PVAc (230,000), and PMMA (110,000).

RESULTS AND DISCUSSION

Diffusivity and equilibrium data were collected above the glass transition temperature for the following six systems: PVAc-chloroform, PVAc-toluene, PVAc-tetrahydrofuran, PMMA-methanol, PMMA-toluene, and polystyrene-carbon disulfide. The sorption equilibrium data for the first two systems were well represented by the Flory-Huggins theory with a single value of χ . A comparison of the activity-weight fraction data for the PVAc-chloroform system with the Flory-Huggins prediction is shown in Figure 1. The diffusivity data for the six systems are presented in Figures 2 and 3 and in Table I. The PVAc-chloroform and PVAc-toluene data and data collected by Kishimoto¹⁹ for the PVAc-methanol system are used to evaluate the correlative and predictive capabilities of the proposed free-volume theory. The PMMA-methanol and PMMA-toluene diffusivity data and PMMA-solvent diffusivity data obtained by Ryskin²⁰ are used to construct a $\gamma \hat{V}_2^* \xi / K_{12}$ vs. solvent molar volume plot for PMMA. Only a limited amount of diffusion coefficient data were collected for

TABLE I
Diffusivity Data for Four Polymer-Solvent Systems

System	Temperature (°C)	Solvent weight percent	$D \times 10^8$ (cm ² /s)
PVAc-tetrahydrofuran	42.6	4.49	0.903
		10.4	7.94
Polystyrene-carbon disulfide	115	1.01	1.40
		2.15	2.50
		3.57	3.63
	140	0.647	5.70
		1.28	6.72
		2.48	12.1
PMMA-toluene	130	2.57	12.6
		1.16	0.208
		4.91	1.06
	140	9.53	17.0
		2.61	1.00
		6.34	8.26
	160	0.410	1.15
		1.16	1.46
		2.00	2.87
2.19		2.83	
3.31		4.96	
0.192		5.05	
PMMA-methanol	120	0.506	5.24
		0.836	6.49
		0.191	8.29
	130	0.487	9.08
		0.746	8.97
		0.304	33.8

the PVAc-tetrahydrofuran and polystyrene-carbon disulfide systems, and no data analysis is carried out for these polymer-penetrant pairs.

The correlative capabilities of the new free-volume theory are illustrated in Figures 2 and 3. All of the diffusivity data for the PVAc-toluene and PVAc-chloroform systems were used to determine D_0 , E , and ξ for each system using a nonlinear regression analysis based on eqs. (1)–(3). The free-volume parameters for these two systems are presented in Table II. It is evident that the theory provides excellent correlations of the diffusivity data for both systems over

TABLE II
Parameters of Free-Volume Theory for Figures 2 and 3

Parameter	Toluene-PVAc system	Chloroform-PVAc system
\hat{V}_1^* (cm ³ /g)	0.917	0.510
\hat{V}_2^* (cm ³ /g)	0.749	0.749
K_{11}/γ (cm ³ /g °K)	2.21×10^{-3}	9.73×10^{-4}
K_{12}/γ (cm ³ /g °K)	4.45×10^{-4}	4.45×10^{-4}
$K_{21} - T_{g1}$ (°K)	-103	-61.2
$K_{22} - T_{g2}$ (°K)	-256	-256
χ	0.75	-0.5
ξ	0.86	0.64
D_0 (cm ² /s)	1.55×10^{-4}	6.12
E (kcal/g-mol)	0.20	7.23

TABLE III
Parameters of Free-Volume Theory for Figures 4 and 5

Parameter	Chloroform-PVAc system	Methanol-PVAc system
\hat{V}_1^* (cm ³ /g)	0.510	0.963
\hat{V}_2^* (cm ³ /g)	0.749	0.749
K_{11}/γ (cm ³ /g °K)	9.73×10^{-4}	1.17×10^{-3}
K_{12}/γ (cm ³ /g °K)	4.45×10^{-4}	4.45×10^{-4}
$K_{21} - T_{g1}$ (°K)	-61.2	-47.9
$K_{22} - T_{g2}$ (°K)	-256	-256
χ	-0.5	^a
ξ	0.65	0.45
D_0 (cm ² /s)	27.7	1.99×10^{-7}
E (kcal/g-mol)	8.07	4.80

^a Not needed because thermodynamic diffusion coefficients are computed.

temperature and concentration ranges for which the diffusion coefficient changes by as much as three orders of magnitude.

The predictive capabilities of the proposed free-volume theory were tested by using the PVAc-chloroform data collected in this study and the PVAc-methanol diffusivity data of Kishimoto.¹⁹ The parameters D_0 , E , and ξ were determined using only four data points for the PVAc-chloroform system and three for the PVAc-methanol system, and the ability of the theory to predict the remainder of the data was evaluated. The calculated free-volume parameters are presented in Table III. Comparisons between the theoretical predictions

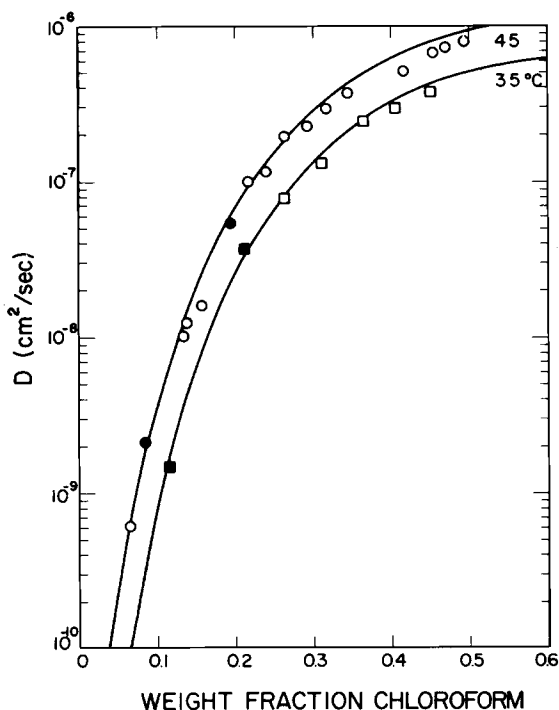


Fig. 4. Test of predictive capabilities of proposed free-volume theory using data for the PVAc-chloroform system. Only data points represented by solid symbols were used to obtain free-volume parameters contained in Table III. (O) 45°C; (□) 35°C.

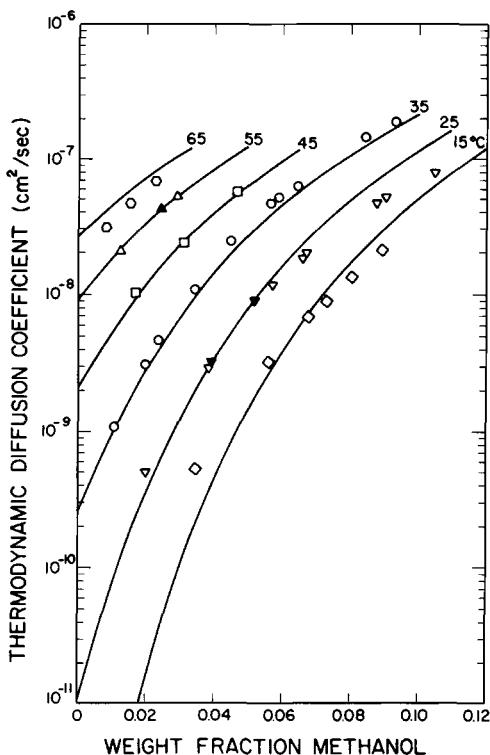


Fig. 5. Test of predictive capabilities of proposed free-volume theory using data for the PVAc—methanol system. Only data points represented by solid symbols were used to obtain free-volume parameters contained in Table III. (○) 65°C; (Δ) 55°C; (□) 45°C; (○) 35°C; (▽) 25°C; (◇) 15°C.

and experimental data are presented in Figures 4 and 5. The data points represented by solid symbols in these figures were used to determine D_0 , E , and ξ . It is fair to conclude that the theory provides good predictions for D over temperature and concentration ranges for which large variations in D occur. The above comparisons provide additional evidence that the proposed free-volume theory is capable of accurately predicting and correlating diffusivity data for concentrated polymer solutions. It should be noted that some of the PVAc-methanol data were obtained at temperatures below the glass transition temperature of the pure polymer. However, it is reasonable to expect that the reported data represent a purely viscous diffusion process (a process for which non-Fickian effects are absent) since the solvent concentrations studied were sufficiently removed from the pure polymer limit.¹⁹ Also, we expect that any branching in the PVAc chain will have a negligible effect on the theoretical predictions unless the branching frequency is unusually high.²¹

Since the parameter ξ represents the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit, it should be possible to determine this parameter from diffusivity data for other solvents in the same polymer. The theory predicts that a plot of $\gamma \hat{V}_2^* \xi / K_{12}$ vs. the molar volume of the solvent jumping unit at 0°K should be linear. Consequently, if polymer-solvent diffusivity data are used to establish the form of this straight line relationship for a given polymer, then $\gamma \hat{V}_2^* \xi / K_{12}$ (and hence ξ) can

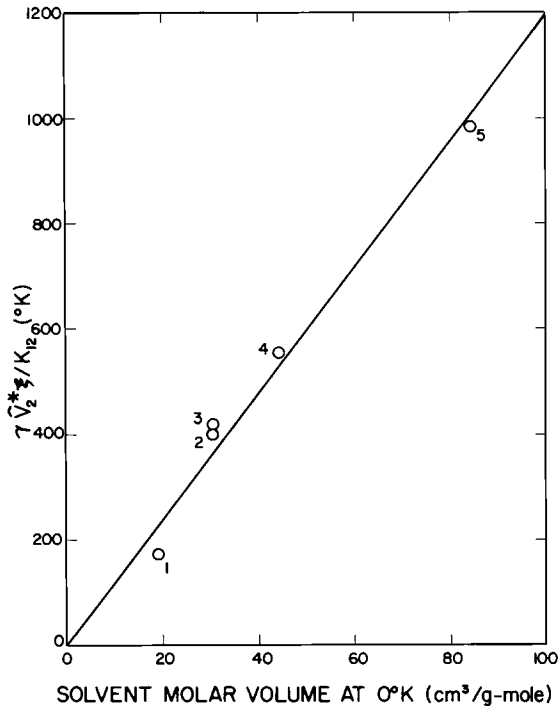


Fig. 6. Variation of $\gamma \hat{V}_2^* \xi / K_{12}$ with solvent molar volume at 0°K for PMMA. (1) Water (Ryskin²⁰); (2) methanol (this study); (3) methanol (Ryskin²⁰); (4) ethanol (Ryskin²⁰); (5) toluene (this study).

be determined for any other solvent diffusing in this polymer if the size of the solvent jumping unit at 0°K is known. In practice, this method is usually restricted to solvents for which the entire molecule performs a jump. Since good linear plots were produced earlier¹⁴ for solvent diffusion in four other amorphous polymers, it is reasonable to expect that this will also be the case for PMMA. The PMMA-solvent diffusivity data of Ryskin²⁰ and those collected in this study were used to compute $\gamma \hat{V}_2^* \xi / K_{12}$ and to construct the $\gamma \hat{V}_2^* \xi / K_{12}$ vs. solvent molar volume plot presented in Figure 6. All four of the solvents considered should jump as single units; their molar volumes at 0°K were calculated using the methods discussed by Haward.¹³ The least-squares line in this figure is a good representation of the data, and good estimates of ξ for other solvents diffusing in PMMA can be derived from this plot.

The above comparisons of data with the theory are encouraging, and we believe that it is fair to conclude that the proposed free-volume theory can provide an accurate description of diffusion in concentrated polymer-solvent systems. However, further evaluation of this theory using new diffusivity data for amorphous polymer-solvent systems is, of course, desirable.

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