

Development of a Predictive Model for Polymer/Solvent Diffusion Coefficient Calculations

F. R. Perieto, M. E. T. Alvarez, W. A. Araujo, M. R. Wolf-Maciel, R. Maciel Filho

School of Chemical Engineering, Separation Process Development Laboratory, State University of Campinas, UNICAMP, 13083-970 Campinas-SP, Brazil

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ABSTRACT: A new calculation procedure for free-volume parameters is considered in this work by using viscosity prediction methods and the Levenberg-Marquardt calculation scheme. All parameters used in the Vrentas–Duda free-volume theory can be estimated from pure component properties. The prediction results are compared with experimental data for some polymer/solvent systems.

The diffusion coefficient calculated by Vrentas–Duda theory can be used in the modeling of membrane separation processes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3544–3551, 2008

Key words: free-volume theory; diffusion coefficients; viscosity; membrane; separation process

INTRODUCTION

The diffusion of small molecules (gases or liquids) in polymeric solids is an important subject being essential for designing and optimizing separation processes as pervaporation and vapor permeation. According to the solution-diffusion model, the knowledge of diffusion coefficient is required to calculate the permeation flux and the downstream composition in the membrane process. Various diffusion models based on free-volume approach have been proposed in the open literature^{1,2} to correlate and to predict diffusion coefficients of solvents in polymers. These theories can achieve predictive status in the future, because most of the required parameters may already be obtained from pure component properties. All model parameters can be estimated without the knowledge of any experimental diffusion data. Determinations of the free-volume model parameters^{1,2} and limitations of the theory were considered in this work. This work also shows a comparative analysis considering group contribution methods and experimental correlations to predict viscosity of solvents and the parameters of free volume. The theoretical results were compared with experimental data available from literature.

METHODOLOGY

The volume of a liquid can be viewed as consisting of two parts: the volume occupied by the molecules

Correspondence to: M. R. Wolf-Maciel (wolf@feq.unicamp.br).

themselves and the empty space between the molecules, which is commonly referred as the free volume. Only the portion that is continuously redistributed by thermal fluctuations is available for molecular transport. This part of the free volume is denoted by hole-free volume, whereas the remainder is termed as the interstitial-free volume.³ The transport mechanism is controlled by the hole-free volume. Molecular transport according to the free-volume theory is probably governed by the occurrence of two events: (1) a hole of sufficient size appears adjacent to a molecule and (2) the molecule has enough energy to jump into the void.³

According to the free-volume diffusion model developed by Vrentas and Duda,^{1,4} the solvent self-diffusion coefficient, D_{11} , is given by eq. (1) and the polymer/solvent binary mutual-diffusion coefficient, D_{12} , is expressed by eq. (2), with subscripts 1 and 2 referring to the solvent and polymer, respectively:

$$D_{11} = D_0 e^{(-E/RT)} e^C \quad (1)$$

$$D_{12} = D_{11} (1 - \phi_1)^2 (1 - 2\chi\phi_1) \quad (2)$$

where:

$$C = \left(\frac{-(\omega_1 V_1^* + \varepsilon \omega_2 V_2^*)}{\omega_1 \left(\frac{K_{11}}{\gamma} \right) (K_{21} - T_{g1} + T) + \omega_2 \left(\frac{K_{12}}{\gamma} \right) (K_{22} - T_{g2} + T)} \right) \quad (3)$$

E (cal/mol) are the parameters necessary to the calculation. Here, χ is determined by correlating solubility data with Flory-Huggins equation or using UNIFAC methodology applied to polymeric solution according to Oishi and Prausnitz.⁵ Of these 10 parameters, six are pure component properties; the remaining four parameters (ε , D_0 , K_{11}/γ , and $K_{21} - T_{g1}$) can be predicted by using the method of Ju et al.,⁶ the nonlinear regression of viscosity experimental data or through viscosity group contribution method. Viscosity data were obtained from experimental data correlations from literature.⁷ Determination of liquid viscosity from group contribution methods available in the open literature^{7,8} was also studied and applied in this work. Because the viscosity-temperature relationship shows its largest curvature at reduced temperatures, low temperature data are essential to estimate solvent free-volume parameters accurately.⁹ It is essential that these correlations can predict the behavior of viscosity-temperature curve close to the melting point of the solvents.

ESTIMATION OF FREE-VOLUME PARAMETERS

Methods for estimating free-volume parameters to predict diffusion profile are discussed in this section.

The critical volumes, V_1^* , V_2^* , represent the minimum specific hole-free volume required to allow the solvent and the polymer molecule to take a diffusive jump and they were estimated as the specific volumes of solvent (V_1^*) and polymer (V_2^*) at 0 K, respectively. In this work, the group contribution method of Sugden¹⁰ was used to calculate them.

Doolittle¹¹ derived the empirical Vogel viscosity model from free-volume concepts [see eq. (4)]. The free volume referred in eq. (4) is interpreted by Vrentas and Duda as the hole-free volume, because viscosity is considered to be a transport property and so governed by this parameter. Low-temperature viscosity data must be available to reflect accurately the inherent nonlinearity of eq. (4).

$$\ln \eta_1 = \ln A_1 + \frac{\frac{V_1^*}{K_{11}/\gamma}}{(K_{21} - T_{g1}) + T} \quad (4)$$

where A_1 is a constant preexponential factor and η_1 is the solvent viscosity.

The WLF equation (Williams-Landel-Ferry), developed by Williams et al.,¹² has become the standard relation in correlating viscosity with temperature for polymers and solvents. The free-volume parameters for polymers, K_{12}/γ , $K_{22} - T_{g2}$, are related to WLF equation, according to Zielinski and Duda:³

$$\frac{K_{12}}{\gamma} = \frac{V_2^*}{2.303C_{12}^{\text{WLF}}C_{22}^{\text{WLF}}} \quad (5)$$

$$K_{22} = C_{22}^{\text{WLF}} \quad (6)$$

Parameters C_{12}^{WLF} and C_{22}^{WLF} have been tabulated for a large number of polymers in the open literature.^{3,13} Parameters K_{11}/γ , $K_{21} - T_{g1}$, D_0 , and E were obtained from nonlinear regression of eq. (7).⁹

$$\ln\left(\frac{1.03087 \times 10^{-10} V_{c1}^{2/3} T}{\eta_1 \text{PM}_1 V_1}\right) = \ln(D_0) - \frac{E}{RT} - \frac{\frac{V_1}{K_{11}/\gamma}}{K_{21} - T_{g1} + T} \quad (7)$$

where V_{c1} and PM_1 are the critical molar volume and molecular weight of the solvent, respectively and 1.03087×10^{-9} is a constant. R is the Universal Gas Constant (1.987 cal/mol K). The temperature-dependent parameters in this equation are η_1 (cP) and V_1 (cm³/g), the viscosity and specific volume of the pure solvent, respectively. The correlation of specific volume presented in Perry and Green¹⁴ was used for calculating the specific volume of the pure solvent.

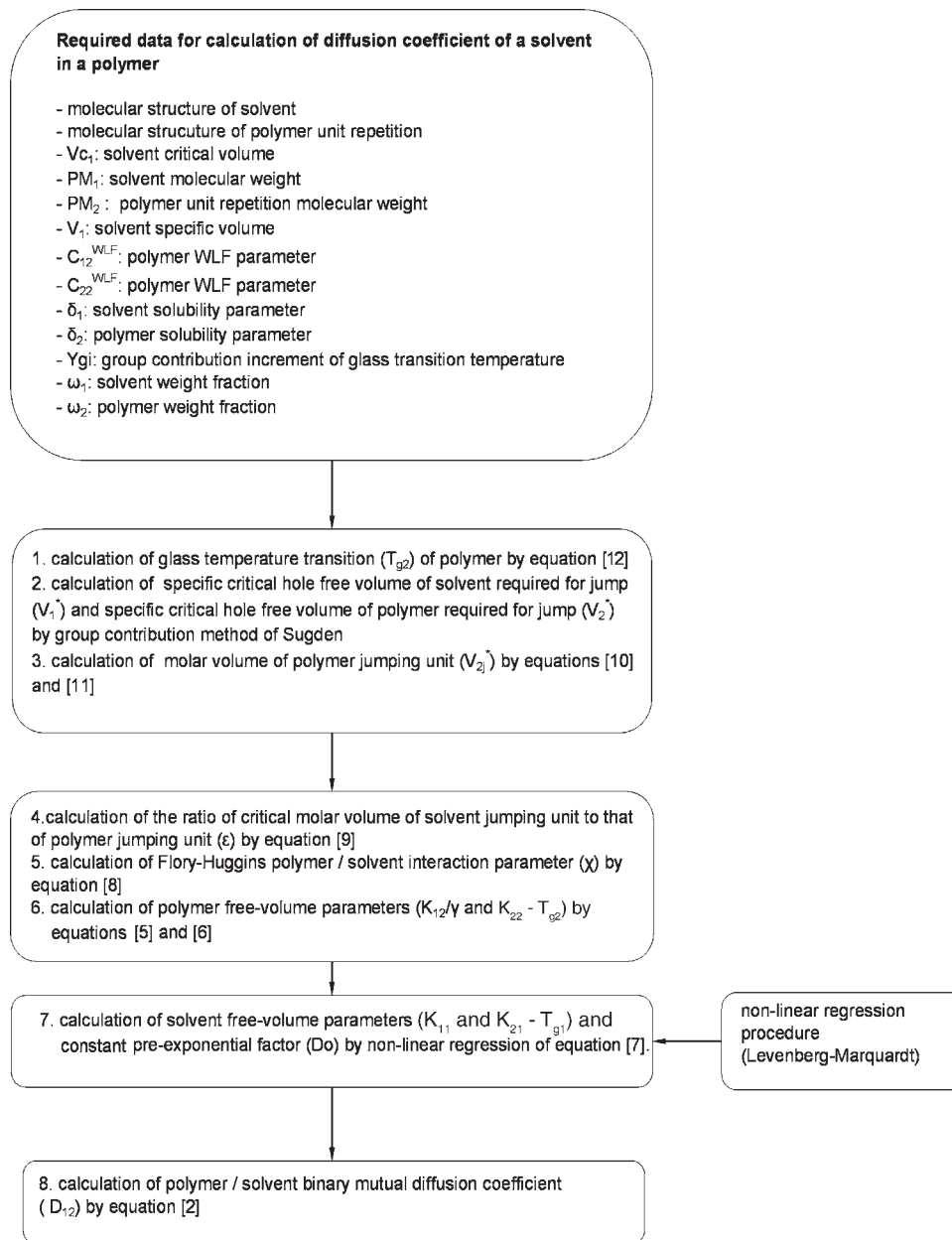
For calculation of pure solvent viscosity, it was applied the correlation of liquid viscosity data from Reid et al.⁷ Moreover, by keeping the predictive nature of the methodology, a relatively recent group contribution method developed by Hsu et al.⁸ and Orrick and Erbar (summarized in Reid⁷) were used to estimate the solvent viscosity. After that, a comparative analysis was carried out with viscosities obtained from correlations based on experimental data, which will be shown in the next section. The influence of viscosities predicted by group contribution methods on the free-volume parameters will also be shown.

According to Hong,⁹ the assumption of negligible energy ($E \approx 0$) can be incorporated into eq. (7) and the remaining parameters obtained from the nonlinear regression were K_{11}/γ , $K_{21} - T_{g1}$, and D_0 . The Levenberg-Marquardt^{15,16} method for nonlinear regression was used, because this is a typical problem of nonlinear unconstrained minimization, where this method is one of the most indicated.

The polymer/solvent interaction parameter χ was determined from a semiempirical equation developed by Bristow and Watson:¹⁷

$$\chi = 0.35 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (8)$$

where V_1 is the solvent molar volume and δ_1 , δ_2 are the solubility parameters of the solvent and polymer, respectively.



The parameter ϵ is defined as the ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit.⁹

$$\epsilon = \frac{V_1^* PM_1}{V_{2j}^*} \quad (9)$$

$$V_{2j}^* = 0.0925T_{g2} + 69.47, \quad \text{if } T_{g2} < 295 \text{ K} \quad (10)$$

$$V_{2j}^* = 0.6224T_{g2} - 86.95, \quad \text{if } T_{g2} \geq 295 \text{ K} \quad (11)$$

where V_{2j}^* is the molar volume of the polymer jumping unit and T_{g2} is the glass transition temperature. The glass transition temperature of polymer was

obtained by the group contribution method of Van Krevelen.¹⁸

$$T_{g2} = \frac{\sum_i Y_{gi}}{PM_2} \times 1000 \quad (12)$$

where Y_{gi} is the group contribution increment of glass transition temperature and PM_2 is the molecular weight of the polymer unit repetition.

These equations for the parameters were chosen because they are the best ones to deal with the relationships of the polymer-solvent free volume.

A detailed algorithm of the calculation procedure is represented in Figure 1.

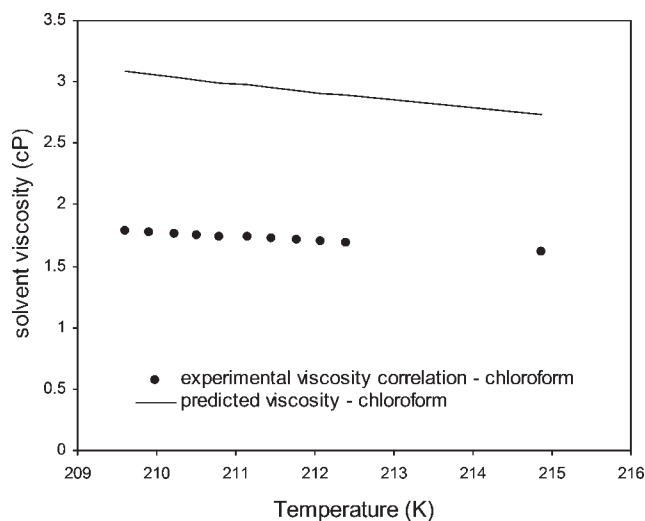


Figure 2 Experimental data and theoretical predictions of viscosity of chloroform.

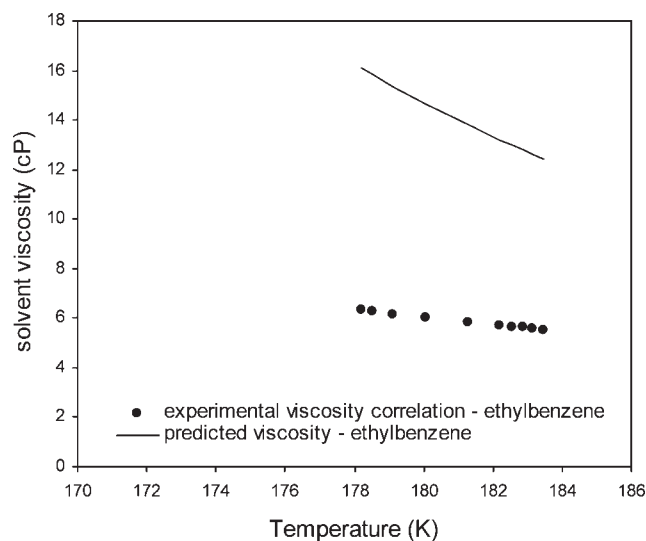


Figure 4 Experimental data and theoretical predictions for viscosity of ethylbenzene.

RESULTS AND DISCUSSION

Four systems were considered in this work: poly(vinyl acetate)/chloroform, poly(vinyl acetate)/toluene, poly(styrene)/ethylbenzene, and poly(styrene)/benzene. These systems were chosen to validate the studies of this work because of the availability of experimental data in the open literature.^{3,9} The results obtained in this work were based on the prediction of the free-volume parameters through a correlation of viscosity using experimental data or on group contribution method to predict solvent viscosity for determining the volume-free parameters. Both results agree well with experimental data of diffusion coefficients, despite the differences between viscosity values obtained.

Figures 2 and 3 present the viscosities of chloroform and toluene obtained by the experimental data correlation⁷ and by the group contribution method.^{7,8} The group contribution method of Orrick and Erbar (summarized in Reid⁷) was used to predict the viscosity of chloroform in the range close to its normal freezing point. The group contribution method of Hsu et al.⁸ was used to predict the viscosity of toluene in the range close to its normal freezing point.

Figures 4 and 5 present viscosities of ethylbenzene and of benzene obtained by experimental data correlation⁷ and by group contribution method.^{7,8} The group contribution method of Orrick and Erbar⁷ was used to predict the viscosity of benzene in the range

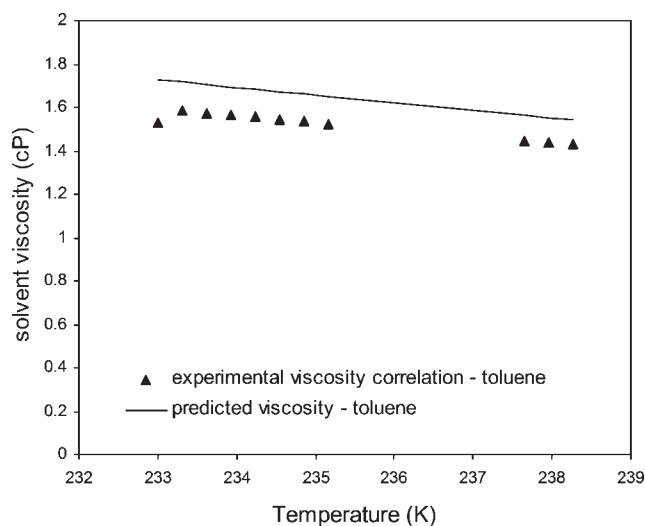


Figure 3 Experimental data and theoretical predictions for viscosity of toluene.

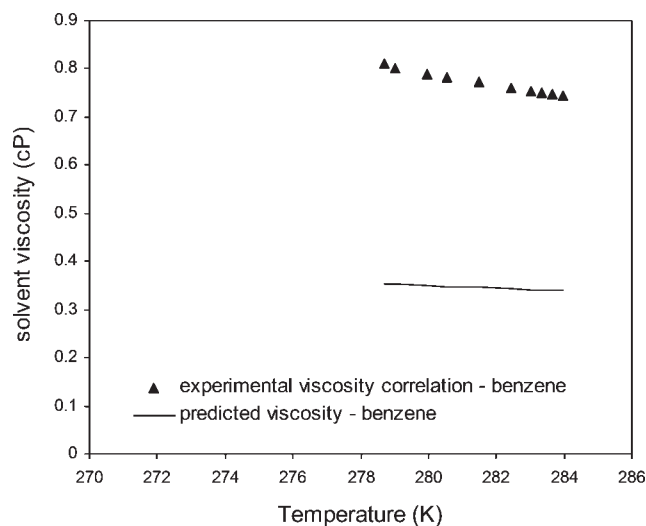


Figure 5 Experimental data and theoretical predictions for viscosity of benzene.

TABLE I
Parameters Used in the Diffusion Coefficient Predictions

Parameter	PVAc/ chloroform	PVAc/ toluene	PS/ ethylbenzene	PS/ benzene
V_1^* (cm ³ /g)	0.550	0.920	0.946	0.914
V_2^* (cm ³ /g)	0.748	0.748	0.850	0.850
T_{g2} (K)	302.00	302.00	373.00	373.00
$K_{12}/\gamma \times 10^4$ (cm ³ /g K)	4.480	4.480	5.823	5.823
$K_{22} - T_{g2}$ (K)	-255.170	-255.170	-327.00	-327.00
$K_{11}/\gamma \times 10^4$ (cm ³ /g K)	4.524	9.831	9.681	12.03
$K_{21} - T_{g1}$ (K)	1.305	-40.170	-45.37	-9.58
$D_0 \times 10^3$ (cm ² /s)	1.181	0.877	0.837	0.494
χ	0.362	0.362	0.710	0.710
ε	0.651	0.851	0.692	0.491
E (cal/mol)	0	0	0	0

close to its normal freezing point. The group contribution method of Hsu et al.⁸ was used to predict the viscosity of ethylbenzene in the range close to its normal freezing point.

The parameters used in the diffusion coefficient predictions are shown in Table I. All parameters were estimated according to eqs. (5)–(12), without the need of any diffusion data. PVAc is poly(vinyl acetate) and PS is poly(styrene).

Figures 6 and 7 present the diffusion coefficient calculated for poly(vinyl acetate)/chloroform system at 308 and 318 K in function of the respective solvent weight fraction. The prediction results agree quite well with the experimental data and with the theoretical predictions from literature.³ The determination of free-volume parameters using viscosity data through group contribution methods resulted in improved diffusion coefficient predictions, closer to the experimental data.

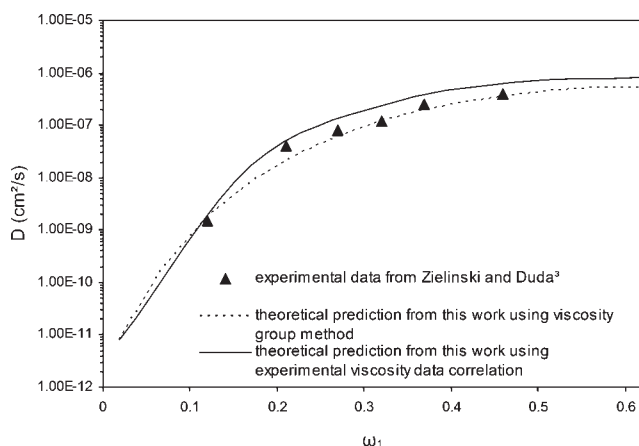


Figure 6 Experimental data and theoretical predictions for mutual-diffusion coefficient of chloroform in poly(vinyl acetate) at 308 K.

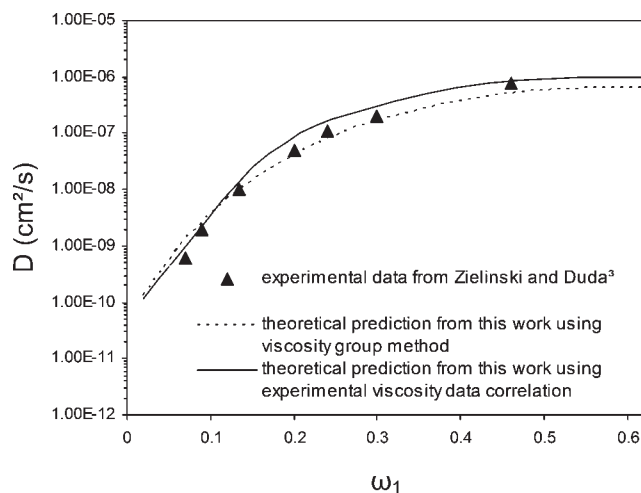


Figure 7 Experimental data and theoretical predictions for mutual-diffusion coefficient of chloroform in poly(vinyl acetate) at 318 K.

Figures 8 and 9 represent the diffusion coefficient calculated for poly(vinyl acetate)/toluene system at 313 and 353 K, respectively. The prediction results also agreed quite well with experimental data and theoretical predictions from literature.

Figures 10 and 11 present the diffusion coefficient calculated for poly(styrene)/ethylbenzene system at 388 and 403 K.

Figures 12 and 13 present the self-diffusion coefficient calculated for poly(styrene)/benzene system at 333 and 373 K.

A sensitivity analysis has been carried out for each parameter to check which parameters have more influence on the diffusion coefficient. The poly(vinyl acetate)/chloroform at 308 K was used in this analysis. The value of each parameter in Table I was decreased to 50% in relation to the original value, while setting the other parameters constant. The

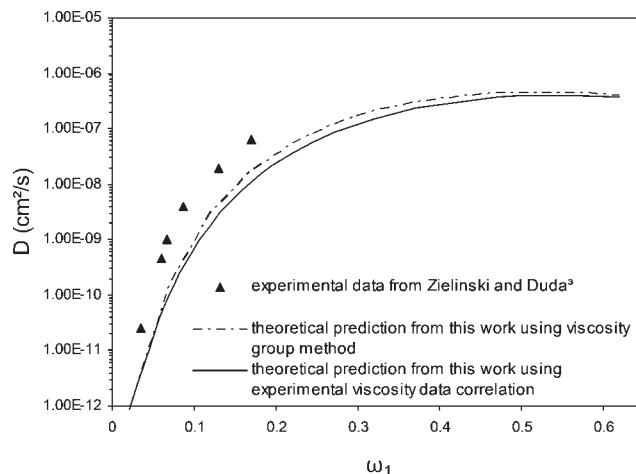


Figure 8 Experimental data and theoretical predictions for mutual-diffusion coefficient of toluene in poly(vinyl acetate) at 313 K.

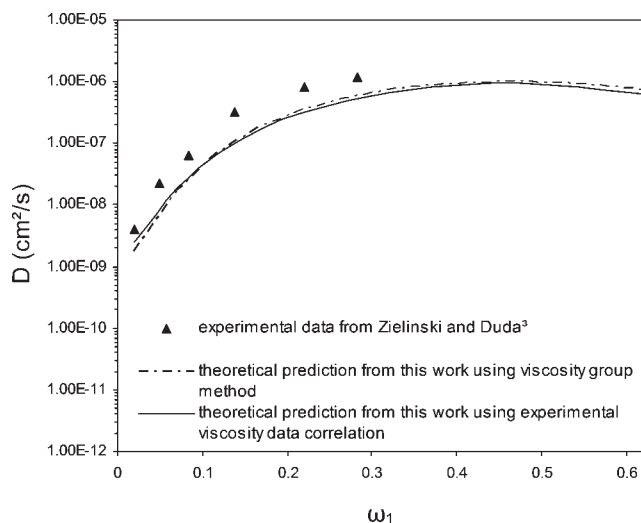


Figure 9 Experimental data and theoretical predictions for mutual-diffusion coefficient of toluene in poly(vinyl acetate) at 353 K.

entire range of composition was considered in this analysis. A sensitivity analysis has been introduced as follows.⁹

$$F = \log \frac{D_v}{D_{\text{reference}}} \quad (13)$$

where D_v is the prediction of the mutual-diffusion coefficient using a parameter value, which has been varied from a reference value, $D_{\text{reference}}$, which is calculated from eq. (2) for a composition range using the parameter values from Table I.

When the F value of a parameter approaches 0, it means that this parameter is a nonsensitive parameter for predicting diffusion behavior. A negative

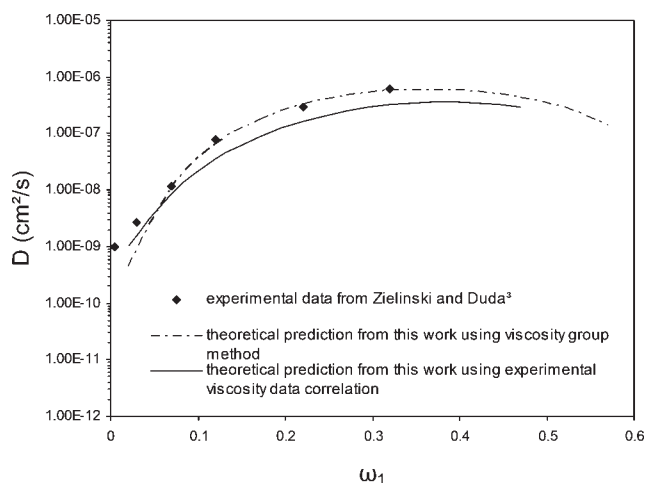


Figure 10 Experimental data and theoretical predictions for mutual-diffusion coefficient of ethylbenzene in poly(styrene) at 388 K.

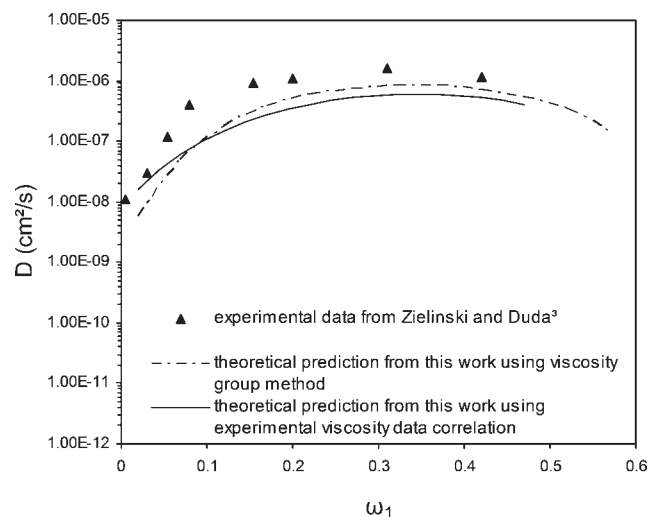


Figure 11 Experimental data and theoretical predictions for mutual-diffusion coefficient of ethylbenzene in poly(styrene) at 403 K.

F value means that the prediction decreases by varying the value of a certain parameter; a positive F value means that the prediction increases by varying the value from a certain parameter. The curves in Figures 14 and 15 show the behavior of each parameter with concentration of solvent in the polymer (ω_1).

It can be noted that $K_{22} - T_{g2}$, K_{12}/γ , K_{11}/γ , V_2^* , and ϵ are the most sensitive parameters in the Vrentas–Duda free-volume theory for this system. V_1^* has small influence. Besides this observation, almost all parameters are more sensitive in the region of low-

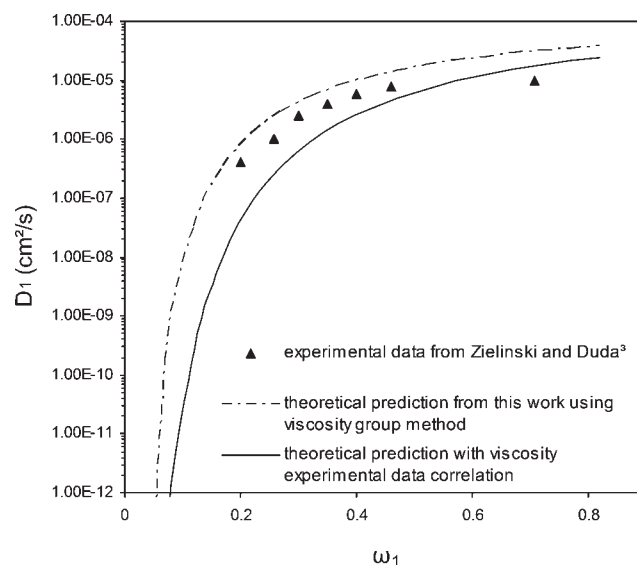


Figure 12 Experimental data and theoretical predictions for self-diffusion coefficient of benzene in poly(styrene) at 333 K.

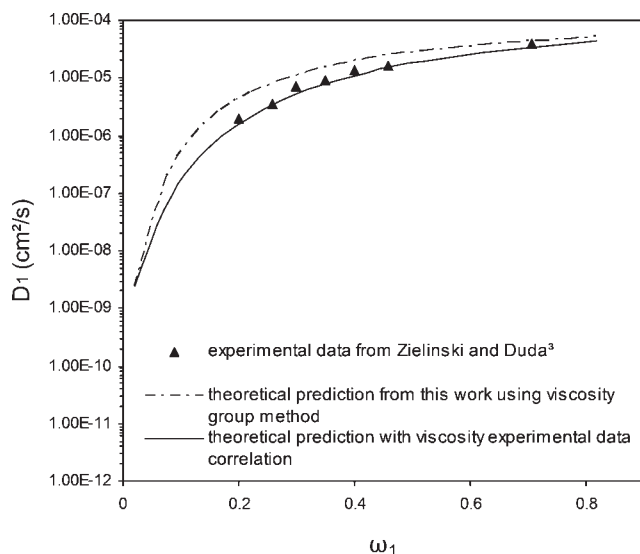


Figure 13 Experimental data and theoretical predictions for self-diffusion coefficient of benzene in poly(styrene) at 373 K.

weight fraction of the solvent, whereas in more concentrated solutions this sensitivity decreases.

CONCLUDING REMARKS

The systems studied suggest that it may be possible to predict diffusion coefficients quite well from solely pure-component data. Determination of the free-volume parameters from viscosity data enables that the model of Vrentas and Duda¹ has fully predictive capacity. Therefore, it is possible to predict the diffusion coefficient of any solvent in the poly-

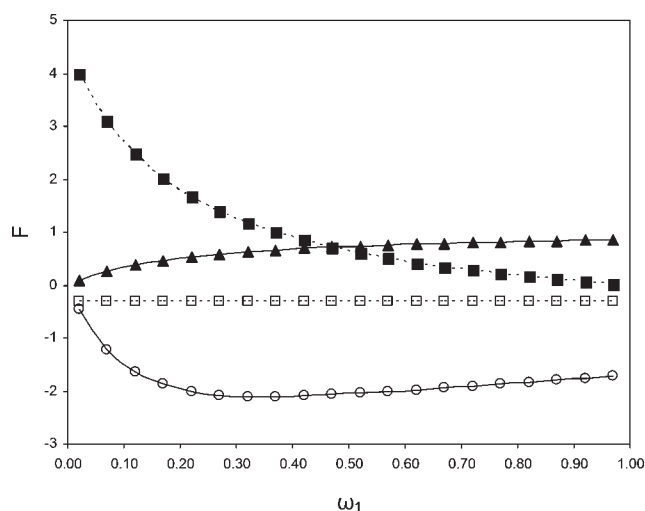


Figure 14 Sensitivity factors (-50% variation) calculated for parameters used for diffusion coefficient prediction versus concentration of solvent in the polymer (ω_1) (\blacksquare — $K_{22} - T_{g2}$, \square — V_2^* , \square — D_0 , \circ — K_{11}/γ). The chloroform-poly(vinyl acetate) system at 308 K was used as reference system.

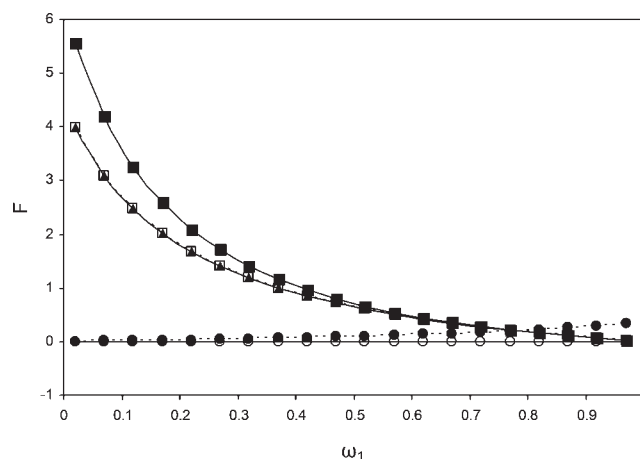


Figure 15 Sensitivity factors (-50% variation) calculated for parameters used for diffusion coefficient prediction versus concentration of solvent in the polymer (ω_1) (\blacksquare — $K_{22} - T_{g2}$, \square — V_2^* , \blacktriangle — K_{12}/γ , \bullet — χ , \circ — $K_{21} - T_{g1}$). The chloroform-poly(vinyl acetate) system at 308 K was used as reference system.

mer without using any diffusivity data to adjust the model. However, it is very important that the density and viscosity data be obtained from low-temperature region, close to the melting normal point of the solvent. Any imprecision in these data will influence the precision of the parameters K_{11}/γ , $K_{21} - T_{g1}$, and D_0 , because these parameters are directly related to the precision of viscosity data used, according to eq. (7). According to the systems studied, the use of group contribution methods to predict solvent viscosity and free-volume parameters resulted in reliable diffusion coefficients.

NOMENCLATURE

A_1	constant preexponential factor (g/cm s)
C_{12}^{WLF}	polymer WLF parameter
C_{22}^{WLF}	polymer WLF parameter (K)
D_{11}	solvent self-diffusion coefficient (cm^2/s)
D_{12}	polymer/solvent binary mutual-diffusion coefficient (cm^2/s)
D_0	constant preexponential factor (cm^2/s)
E	energy required to overcome attractive forces from neighboring molecules (cal/mol)
F	sensitivity factor
F_i	sensitivity factor of parameter i
K_{11}	solvent free-volume parameter ($\text{cm}^3/\text{g K}$)
K_{12}	polymer free-volume parameter ($\text{cm}^3/\text{g K}$)
K_{21}	solvent free-volume parameter (K)
K_{22}	polymer free-volume parameter (K)
PM_1	solvent molecular weight (g/mol)
PM_2	polymer unit repetition molecular weight (g/mol)
R	gas constant (cal/mol K)
T	temperature (K)

T_{g1}	solvent glass transition temperature (K)
T_{g2}	polymer glass transition temperature (K)
V_1^*	specific critical hole-free volume of solvent required for jump (cm^3/g)
V_1	solvent specific volume (cm^3/g)
V_2^*	specific critical hole-free volume of polymer required for jump (cm^3/g)
V_{2j}^*	molar volume of polymer jumping unit (cm^3/mol)
V_c	solvent critical volume (cm^3/g)
Y_{gi}	group contribution increment of glass transition temperature
γ	overlap factor which accounts for shared free volume
δ_1	solvent solubility parameter (cal/cm^3) ^{1/2}
δ_2	polymer solubility parameter (cal/cm^3) ^{1/2}
ε	ratio of critical molar volume of solvent jumping unit to that of polymer jumping unit
η_1	solvent viscosity ($\text{g}/\text{cm} \cdot \text{s}$)
ϕ_1	solvent volume fraction
χ	Flory-Huggins polymer/solvent interaction parameter
ω_1	solvent weight fraction
ω_2	polymer weight fraction

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