

A Modified Vrentas–Duda Model for the Correlation of the Solvent Self-Diffusion Coefficients in Polymer Solutions

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ABSTRACT: A new expression for the specific hole free volume in the Vrentas–Duda (VD) model was proposed, and a modified VD model was developed for the correlation of the solvent self-diffusion coefficients in polymer solutions. The new model gives better correlation for the finite concentration solvent self-diffusion coefficients than the VD model, which also shows better predictions for the infinite dilution solvent self-diffusion coefficients than the latter. The modified VD model takes into account the pressure effects on diffusion coefficients through the pressure dependence of the specific volumes from an existing equation of state, which can be used to predict the pressure dependence of diffusion coefficients with the parameters obtained from atmospheric pressure diffusivity data.

KEY WORDS Free Volume / Diffusion Coefficient / Polymer Solution / Correlation / Prediction /

Diffusion of solvent in polymer solution is important in many polymer processing processes, as most polymeric materials have to be solved in solvents during production and/or processing to get good fluidity, and the solvents need to be removed later, where the rate of diffusion of the solvent through the polymer plays a key role. Therefore, reliable estimation methods of solvent diffusivity in polymer solutions are essential. Theoretical models have been extensively studied, the most commonly used models are those based on the free volume concept,^{1–4} and a recent review on the available estimation methods can be found in the book of Caruthers *et al.*⁵ Most of the existing models were developed mainly to describe the dependence of the diffusion coefficients on temperature and concentration, little attention has been paid to the effect of pressure on diffusion in polymer solutions. For example, the Vrentas–Duda (VD) model,^{3,4} a representative of the free-volume models, is commonly used to correlate and predict the dependence of the diffusion coefficients on temperature and concentration, though it can also be used to describe the pressure effects. As there is a scarcity of pressure-dependent diffusion coefficient data, it is useful to develop a diffusion coefficient model which can predict the pressure effect using the parameters obtained by fitting atmospheric pressure diffusion coefficient data, which is the motivation of this work.

THEORY

Loflin and McLaughlin⁶ proposed the following relation between binary mutual- and the self-diffusion coefficient based on the theoretical work of Bearman:⁷

$$D = \frac{(D_1x_2 + D_2x_1)}{RT} \left(\frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P} \quad (1)$$

where D_1 and D_2 are the self-diffusion coefficient of component 1 and 2, respectively. μ_i and x_i are the chemical potential and mole fraction of component i , respectively. For polymer (D_2)–solvent (D_1) systems where D_1 is much larger than D_2 , Vrentas and Duda³ have shown that in the limit the solvent concentration approaches zero, eq 1 can be approximated by the following expression:

$$D = \frac{D_1x_2}{RT} \left(\frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P} \quad (2)$$

Equation 2 is only rigorously valid in the zero solvent concentration limit, however, as D_2 is usually not known, there are no practical alternatives to eq 2, and it is commonly assumed to be acceptable for all polymer–solvent systems over most concentration range.⁵

Obviously, two models are required to calculate the mutual diffusion coefficient D by eq 2, one is a solvent self-diffusion coefficient model for D_1 , the other is a thermodynamic model for the calculation of the thermodynamic factor, $\left(\frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P}$, and the both models affect the predictive accuracy of D . The thermodynamic factor, $\left(\frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P}$, has been calculated with the Flory's theory⁸ by Vrentas and Duda,⁹ with the Flory–Huggins model¹⁰ by Duda *et al.*,¹¹ and with two predictive UNIFAC-FV type models by Kim and Lee.¹² More recently, an evaluation of the predictive capability of the existing group contribution thermodynamic

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models for $\left(\frac{\partial\mu_1}{\partial\ln x_1}\right)_{T,P}$ was carried out by us,¹³ which shows that reasonable predictions can be achieved with these models. The predictive thermodynamic models for $\left(\frac{\partial\mu_1}{\partial\ln x_1}\right)_{T,P}$ coupled with an accurate model for D_1 will give good predictions for the mutual diffusion coefficients in polymer solutions.

The Vrentas–Duda Free-Volume Model

The free-volume model for the solvent self-diffusion coefficient proposed by Vrentas and Duda is as follows:^{3,4}

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right) \exp\left[\frac{-(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}/\gamma}\right] \quad (3)$$

and

$$\hat{V}_{FH}/\gamma = \omega_1 \hat{V}_{FH1}/\gamma_1 + \omega_2 \hat{V}_{FH2}/\gamma_2 \quad (4)$$

$$\hat{V}_{FH1} = K_{11}(K_{21} + T - T_{g1}) \quad (5)$$

$$\hat{V}_{FH2} = K_{12}(K_{22} + T - T_{g2}) \quad (6)$$

where D_0 is the pre-exponential factor, E is the critical energy a molecule must obtain in order to overcome the attractive forces holding it to its neighbors. ω_1 and ω_2 are the weight fraction of solvent and polymer, respectively. \hat{V}_i^* is the specific hole free volume of component i required for a jump, ξ is the ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit. \hat{V}_{FH} is the average specific hole free volume of mixture, γ represents an average overlap factor for the mixture, and γ_i represents the overlap factor for the free volume for pure component i . K_{11} , K_{21} , K_{12} , and K_{22} are the free-volume parameters, and T_{g1} and T_{g2} are the glass transition temperature of solvent and polymer, respectively.

The model contains 13 parameters, however, these parameters can be combined into the following 9 groups: K_{11}/γ_1 , $K_{21} - T_{g1}$, K_{12}/γ_2 , $K_{22} - T_{g2}$, \hat{V}_1^* , \hat{V}_2^* , D_0 , E , and ξ . Excepting the parameter E , the other 8 parameters can be estimated from viscosity and density data,^{5,14} however, the predictive accuracy of the VD model with $E = 0$ and the other parameters estimated by the above method is less than satisfying.

Though the VD model can describe the dependence of the diffusion coefficients on pressure, it is normally used to correlate and predict the temperature and concentration dependence of the diffusion coefficients, and all the parameters are normally treated as temperature and pressure independent constants. In this case, the VD model cannot describe the pressure effects as pressure is not a variable in the VD model.

Development of the New Hole Free Volume Expression

The hole free volume in the Vrentas–Duda model is, as shown in eqs 4–6, a linear function of temperature and concentration. Though the pressure effects can be taken into account by using pressure-dependent free-volume parameters, T_{g1} and T_{g2} , they are usually treated as pressure-independent constants, and the pressure effects cannot be incorporated in a simple way. Therefore, a new expression for the hole free volume was developed to incorporate the pressure effect simply and easily as follows.

The specific free volume \hat{V}_F is defined by Vrentas and Duda³ as follows:

$$\hat{V}_F = \hat{V} - \hat{V}_0 = \hat{V} - \hat{V}(0) = \hat{V} - \hat{V}^* \quad (7)$$

where \hat{V} is the specific volume of the equilibrium liquid structure at any temperature, and the specific occupied volume of a liquid \hat{V}_0 is defined to be the specific volume of the equilibrium liquid at 0 K, which is set to be identical to \hat{V}^* of a liquid.³

The \hat{V}_F is usually assumed to consist of two parts as follows:³

$$\hat{V}_F = \hat{V}_{FI} + \hat{V}_{FH} \quad (8)$$

where \hat{V}_{FI} is the specific interstitial free volume and \hat{V}_{FH} is the specific hole free volume, the latter is the quantity which is available for molecular transport.

In this work eq 8 is rewritten as follows:

$$\hat{V}_{FH} = \eta \hat{V}_F \quad (9)$$

where η is a factor between 0 and 1, which represents the percentage of the total free volume that is caused by the formation of holes or vacancies when the temperature is increased from 0 K to a certain temperature.

Upon substitution of eq 7 into eq 9, one obtains:

$$\hat{V}_{FH} = \eta(\hat{V} - \hat{V}^*) \quad (10)$$

Furthermore, substituting eq 10 into eq 4, we obtained a new expression for the hole free volume in a polymer–solvent system as follows:

$$\hat{V}_{FH}/\gamma = \omega_1(\hat{V}_1 - \hat{V}_1^*)\eta_1/\gamma_1 + \omega_2(\hat{V}_2 - \hat{V}_2^*)\eta_2/\gamma_2 \quad (11)$$

Equation 11 can be further rewritten as follows:

$$\hat{V}_{FH}/\gamma = \omega_1(\hat{V}_1 - \hat{V}_1^*)\lambda_1 + \omega_2(\hat{V}_2 - \hat{V}_2^*)\lambda_2 \quad (12)$$

where λ_i , defined as η_i/γ_i , is called herein the “effective free volume factor” of component i , which represents the effective contribution of the free volume to the part that is available for molecular transport. \hat{V}_1 and \hat{V}_2 are the specific volume of solvent and polymer at temperature T and pressure P , respectively.

Substituting eq 12 into eq 3, a modified free volume model for solvent self-diffusion coefficient was obtained as follows:

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right) \times \exp\left[\frac{-(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\omega_1(\hat{V}_1 - \hat{V}_1^*)\lambda_1 + \omega_2(\hat{V}_2 - \hat{V}_2^*)\lambda_2}\right] \quad (13)$$

The model contains 7 parameters, \hat{V}_1^* , \hat{V}_2^* , D_0 , E , ξ , λ_1 , and λ_2 . As the estimation method for \hat{V}_1^* and \hat{V}_2^* proposed by Zielinski and Duda¹⁴ is a good approximation, we treat \hat{V}_1^* and \hat{V}_2^* as known parameters estimated by the method of Zielinski and Duda¹⁴ to reduce the number of parameters to be regressed, and the other 5 parameters have to be regressed by fitting experimental data.

The specific volumes of solvents and polymers are required in the new model, and the simplified hole theory equation of state (SHT EOS) developed by us in our previous work¹⁵ was adopted in this work. Details of the EOS are as follows:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{(y\tilde{V})^{1/3}}{(y\tilde{V})^{1/3} - 0.9165y} + \frac{2y}{\tilde{T}(y\tilde{V})^2} [1.1394(y\tilde{V})^{-2} - 1.5317] \quad (14)$$

$$y = 1 - \exp(-c/2s\tilde{T}) \quad (15)$$

For large molecules and polymers, eq 15 can be simplified by the following equation:¹⁵

$$y = 1 - \exp(-0.52/\tilde{T}) \quad (16)$$

where $3c$ is the number of external degrees of freedom per molecule, s is the number of segments in a molecule. The reduced variables are defined as follows:

$$\tilde{T} = T/T^* \quad (17)$$

$$\tilde{P} = P/P^* \quad (18)$$

$$\tilde{V} = V/V^* \quad (19)$$

where T^* , P^* , and V^* are three substance-dependent characteristic parameters, which can be obtained by fitting the pure substance PVT data, which are already available for a large number of solvents and polymers.^{15–17} The parameters used in this work are listed in Table I.

Obviously, the new model can describe the pressure dependence of diffusivity in terms of the pressure dependence of the specific volumes of the solvent and polymer from an existing equation of state. Furthermore, the temperature and pressure dependence of the hole free volume in the new model is not linear, which may make the model give better description of the solvent diffusion coefficients as a function of temperature, concentration and pressure.

Table I. The characteristic parameters of the SHT EOS for the substances used in this work

Substance	Characteristic parameters			Source
	T^* K	P^* MPa	V^* cm ³ g ⁻¹	
Polystyrene	3976	414.8	0.923	15
Polyisobutylene	3601	394.9	1.053	15
Poly(methyl methacrylate)	3129	722.5	0.766	^a
Poly(<i>n</i> -butyl methacrylate)	2967	530.3	0.882	15
Benzene	2363	448.0	0.989	16
Toluene	2339	426.0	1.006	16
Cyclohexane	2379	356.0	1.131	16
Dodecane	2128	438.0	1.154	16
Acetone	1624	627.8	0.996	17
Methyl ethyl ketone	1715	612.4	0.999	17
Ethylbenzene	2025	595.0	0.982	17

^aThe parameters are regressed by this work.

Finally, it should be pointed out that Vrentas and Duda⁹ has used the Flory's theory⁸ to calculate the hole free volume of mixture. In their expression the specific volume of mixture is required,⁹ however, the required interaction parameters for the Flory's theory are not available for many polymer–solvent systems.¹¹ Therefore, the method has limited application. On the other hand, in the new model the specific volume of mixture is avoided by adopting an alternative expression for the hole free volume, where only pure substance parameters of the SHT EOS are required, which are available for many polymers and solvents.

RESULTS AND DISCUSSION

Correlation of the Finite Concentration Solvent Self-Diffusion Coefficients

As a first step to test the modified model, and compare with the original VD model, we used the models to correlate the finite concentration solvent self-diffusion coefficients, and a total of 11 polymer–solvent systems were collected from the literature.^{18–20} For the new model the two specific volume parameters, \hat{V}_1^* and \hat{V}_2^* , were estimated with the method adopted by Zielinski and Duda,¹⁴ while the other five parameters were regressed by fitting the experimental diffusion data. Therefore, the new model is actually a five-parameter model. To have a common comparison basis, the VD model was also treated as a five-parameter model, with K_{11}/γ_1 , $K_{21} - T_{g1}$, D_0 , E , and ξ being adjustable parameters obtained by fitting the experimental diffusion data. The other four parameters, \hat{V}_1^* , \hat{V}_2^* , K_{12}/γ_2 , and $K_{22} - T_{g2}$, were treated as known parameters, which have been estimated by Zielinski and Duda.¹⁴ The relevant parameters obtained by Zielinski and Duda¹⁴ are listed in Table II.

Table II. The characteristic parameters of Vrentas–Duda model for the substances used in this work¹⁴

Substance	\hat{V}_2^* cm ³ g ⁻¹	$(K_{12}/\gamma_2) \times 10^4$ cm ³ g ⁻¹ K ⁻¹	$K_{22} - T_{g2}$ K	\hat{V}_2^* cm ³ g ⁻¹
Polystyrene	0.850	5.82	-327.0	
Polyisobutylene	1.004	2.51	-100.6	
Poly(methyl methacrylate)	0.788	3.05	-301.0	
Poly(<i>n</i> -butyl methacrylate) ^a	0.862 ^b	–	–	
Benzene				0.901
Toluene				0.917
Cyclohexane				1.043 ^b
Dodecane				1.102 ^b
Acetone				0.943
Methyl ethyl ketone				0.999 ^b
Ethylbenzene				0.946

^aNo Vrentas–Duda model parameters available for Poly(*n*-butyl methacrylate). ^bThe \hat{V}_i^* was estimated in this work with the same method used by Zielinski and Duda.¹⁴

Table III. The correlated results

System	Temp. range	No. of data points	AAD [*]		Data source
	K		this work	Vrentas–Duda	ref.
Polystyrene+Benzene	298–373	48	8.7	11.4	18
Polystyrene+Toluene	298–388	143	6.8	10.9	19
Polystyrene+Ethylbenzene	303–343	20	22.2	26.6	20
Polystyrene+Methyl ethyl ketone	298	7	3.2	5.5	21
Polystyrene+Cyclohexane	331–373	20	14.6	17.9	22
Polystyrene+Dodecane	378–413	12	7.2	9.3	23
Polyisobutylene+Benzene	343.4	12	4.3	5.6	24
Polyisobutylene+Toluene	298–368	48	8.0	14.0	25
Poly(methyl methacrylate)+Acetone	296	14	15.4	17.9	26
Poly(methyl methacrylate)+ Methyl ethyl ketone	299	9	2.1	4.1	27
Poly(<i>n</i> -butyl methacrylate)+ Methyl ethyl ketone	299	9	5.8	6.1	28
System average			8.9	11.8	

$$*AAD = \frac{1}{N} \sum \left| \frac{D_1^{\text{Calc}} - D_1^{\text{Exp.}}}{D_1^{\text{Exp.}}} \right| \times 100$$

The correlated results are shown in Table III. The new model gives better correlative accuracy than the VD model. The overall average absolute deviation (AAD) for the new model is 8.9% against 11.8% for the VD model. It should be pointed out that for Poly(*n*-butyl methacrylate) (PBMA) +Methyl ethyl ketone (MEK) system, the VD model is treated as a 7-parameter model, because the K_{12}/γ_2 and $K_{22} - T_{g2}$ for PBMA are not available, we simply treated them as two additional parameters. The parameters obtained for the new model are reported in Table IV. The parameters seem physically meaningful except for the PBMA-MEK system, where the parameter λ_2 is negative, which means the hole free volume contribution of PBMA is negative. This also happened in the VD model, where $K_{22} - T_{g2} = -446.9$ K, which also gives a negative hole free volume value of PBMA at the tem-

perature used (299 K). It should be further pointed out that for the VD model, the $K_{22} - T_{g2}$ for Polystyrene (PS) is commonly adopted as -327 K as shown in Table II, which gives negative V_{FH2} for PS-solvent systems when the temperature is lower than 327 K. A negative V_{FH2} is of course physically no meaning.

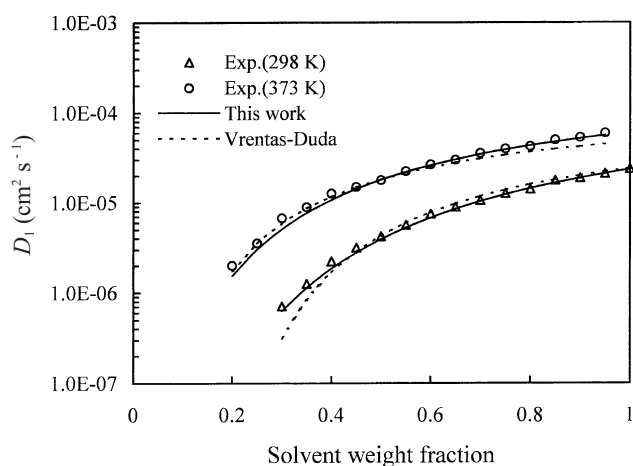
The calculated and the experimental concentration dependence of the solvent self-diffusion coefficients of Polystyrene + Benzene system at 298 and 373 K are shown in Figure 1. Both the two models show correct trend, however, they behave differently due to the difference in the hole free volume expressions.

Prediction of the Infinite Dilution Solvent Self-Diffusion Coefficient

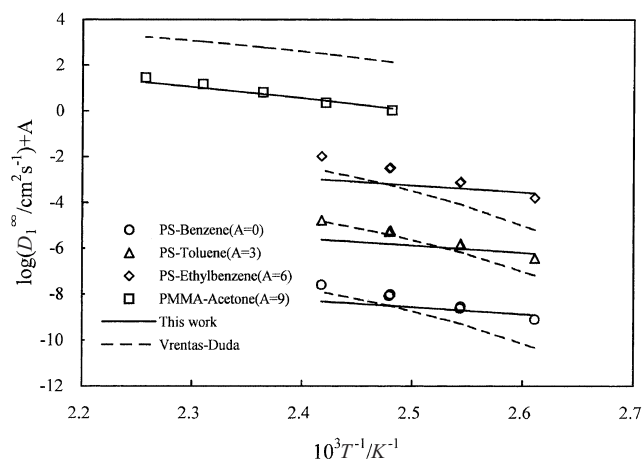
As a second step to test the model, it was used to predict the infinite dilution solvent self-diffusion coeffi-

Table IV. The characteristic parameters for the new model

System	$D_0 \times 10^4$ $\text{cm}^2 \text{s}^{-1}$	E J mol^{-1}	λ_1	λ_2	ξ
Polystyrene+Benzene	6.37	2924	1.825	0.601	0.144
Polystyrene+Toluene	4.98	3093	2.119	0.571	1.129
Polystyrene+Ethylbenzene	1.235	899.2	2.033	0.901	1.799
Polystyrene+Methyl ethyl ketone	2.81	743.0	1.389	0.840	1.170
Polystyrene+Cyclohexane	9.05	97.1	1.563	0.901	1.390
Polystyrene+Dodecane	89.1	9907	1.220	0.885	1.520
Polyisobutylene+Benzene	1.879	193.1	2.273	2.273	1.462
Polyisobutylene+Toluene	1.493	150.3	2.315	1.730	1.599
Poly(methyl methacrylate)+Acetone	3.089	2519	1.852	1.279	1.574
Poly(methyl methacrylate)+ Methyl ethyl ketone	1.425	139.7	1.718	0.656	1.268
Poly(<i>n</i> -butyl methacrylate)+ Methyl ethyl ketone	11.90	4195	1.266	-1.25	0.11

**Figure 1.** The concentration dependence of the solvent self-diffusion coefficients for Polystyrene + Benzene system.

coefficients using the parameters obtained by fitting the finite concentration diffusion data. This is a more serious test of the model, as it is more difficult to calculate the infinite dilution diffusion coefficients accurately. A total of 4 polymer–solvent systems were collected from the literature,^{29,30} and the predicted results of the new model are shown in Figure 2. Parallel calculations were also carried out for the VD model, and the results are also reported in Figure 2. The new model gives slightly better predictions than the VD model in general, however, the VD model shows better temperature-dependence trend. Excepting the Poly(methyl methacrylate) + Acetone system, it seems that the new model is not enough to give good predictions in the whole temperature range tested, which is also the case for the VD model. On the other hand, it is interesting to see that the VD model gives good predictions at high temperatures, while the new model is much better at low temperature levels, a combination of the two expressions for the specific hole free volume may do a good job in a wide temperature

**Figure 2.** The predicted and experimental infinite dilution solvent self-diffusion coefficients vs. temperature.

range.

Prediction of the Pressure Dependence of the Solvent Self-Diffusion Coefficient

An advantage of the new model is that it can describe the pressure dependence of the diffusion in polymer solutions using parameters obtained from atmospheric pressure diffusivity data, which is both theoretical and practical interest. As there are no pressure-dependent diffusion data for polymer solutions available, we can only use the model to predict the pressure dependence behavior, and a quantitative comparison of the model predictions with experimental data is not possible. The system Polystyrene + Toluene is selected as an example to show the predictive results of the model, where calculations for three concentrations, say $\omega_1 = 0.1$, $\omega_1 = 0.5$, and $\omega_1 = 0.9$, were carried out at 350 K. It should be pointed out that all the parameters used are the same as obtained before, therefore, the pressure dependence of the diffusion coefficients is only con-

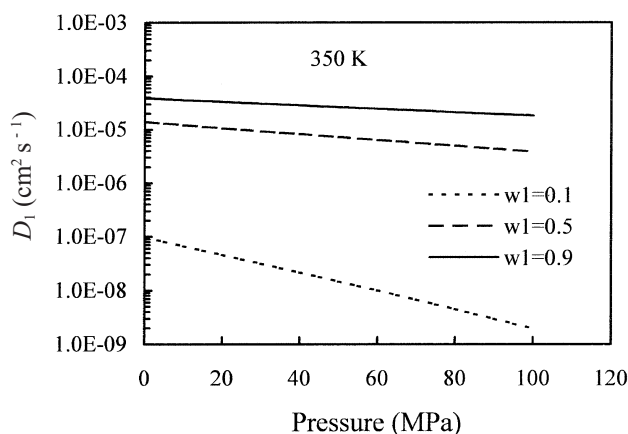


Figure 3. The pressure dependence of the solvent self-diffusion coefficients for Polystyrene + Toluene system at 350 K.

tributed by the pressure dependence of the specific volumes. The predicted results are shown in Figure 3. Obviously, the solvent self-diffusion coefficient decreases with increasing pressure at constant temperature and concentration, which is consistent with the theoretical analysis. Furthermore, it can be seen that the pressure effect on diffusion is not small, for example, the self-diffusion coefficient changes 2 orders of magnitude when the pressure increases from atmospheric pressure to 100 MPa. Therefore, the pressure effect on diffusion in polymer solutions should be taken into account when a process under high pressure is to be designed.

The model predicts correct pressure dependence trend for solvent self-diffusion, however, its predictive accuracy is not very clear at the moment. When experimental data are available, it will be interest to test the quality of the new model.

CONCLUSION

The modified model proposed can describe the pressure dependence of diffusivity in polymer solutions using the parameters obtained from atmospheric pressure diffusivity data, which is very useful for those polymer processing processes operated at high pressures. The correlated results for the finite concentration solvent self-diffusion coefficients, and the predictions for the infinite dilution solvent self-diffusion coefficients show that the new model is more accurate than the five-parameter VD model. The combination of the new model with a group contribution thermodynamic model for $\left(\frac{\partial \mu_1}{\partial \ln x_1}\right)_{T,P}$ may give reliable predictions for the mutual diffusion coefficients in polymer solutions, which is very useful for engineering purposes.

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preciated.

LIST OF SYMBOLS

AAD,	Average absolute deviation defined in Table III
c ,	1/3 of the number of external degrees of freedom per molecule
D ,	Binary mutual diffusion coefficient [$\text{cm}^2 \text{s}^{-1}$]
D_0 ,	The pre-exponential factor [$\text{cm}^2 \text{s}^{-1}$]
D_1 ,	Self-diffusion coefficient of solvent [$\text{cm}^2 \text{s}^{-1}$]
D_2 ,	Self-diffusion coefficient of polymer [$\text{cm}^2 \text{s}^{-1}$]
E ,	Critical energy a molecule must obtain in order to overcome the attractive forces holding it to its neighbors [J mol^{-1}]
K_{11} ,	Solvent free-volume parameter [$\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$]
K_{12} ,	Polymer free-volume parameter [$\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$]
K_{21} ,	Solvent free-volume parameter [K]
K_{22} ,	Polymer free-volume parameter [K]
N ,	The number of data points
P ,	Pressure [MPa]
$\tilde{P}, \tilde{V}, \tilde{T}$,	Reduced pressure, volume, and temperature
P^*, V^*, T^* ,	Characteristic parameters in the SHT EOS [MPa], [$\text{cm}^3 \text{g}^{-1}$], [K]
R ,	Gas constant
s ,	The number of segments in a molecule
T ,	Temperature [K]
T_{g1}, T_{g2} ,	Glass transition temperatures of solvent and polymer, respectively [K]
\hat{V} ,	Specific volume of the equilibrium liquid structure at any temperature [$\text{cm}^3 \text{g}^{-1}$]
\hat{V}_0 ,	Specific occupied volume of a liquid [$\text{cm}^3 \text{g}^{-1}$]
\hat{V}_F ,	Specific free volume [$\text{cm}^3 \text{g}^{-1}$]
\hat{V}_{FH} ,	Specific hole free volume [$\text{cm}^3 \text{g}^{-1}$]
\hat{V}_{FHi} ,	Specific hole free volume of component i [$\text{cm}^3 \text{g}^{-1}$]
\hat{V}_{FI} ,	Specific interstitial free volume [$\text{cm}^3 \text{g}^{-1}$]
\hat{V}_i^* ,	Specific hole free volume of component i required for a jump [$\text{cm}^3 \text{g}^{-1}$]
$\hat{V}(0)$,	Specific volume of the equilibrium liquid at 0 K [$\text{cm}^3 \text{g}^{-1}$]
x_i ,	Mole fraction of component i
y ,	The occupied site fraction

Greek letters

γ , Overlap factor

η ,	Factor defined by eq 9
λ ,	Effective free volume factor
μ_i ,	Chemical potential of component i
ξ ,	The ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit
ω_i ,	Weight fraction

Subscripts

i,	Component i
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Superscripts

Calc.,	Calculated value
Exp.,	Experimental value
∞ ,	Infinite dilution

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