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Testing free volume theory for penetrant diffusion in rubbery polymers

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Abstract

Vrentas and Vrentas (Eur Polym J, 34 (1998) 797) have provided a method of evaluating diffusion coefficients using free volume theory, wherein all parameters can be estimated from the available experimental physical data or best estimates from approximate correlations (e.g. from a knowledge of the density, isothermal expansion coefficient, etc.). This method is tested using data for diffusion of methyl methacrylate and butyl methacrylate monomers in mixtures of the monomer and both polymers above the glass transition, over a range of polymer weight fraction and temperature (above T_g) (Macromolecules, 31 (1998) 7835). It was found that the predictions are reasonable for the well-studied MMA/PMMA system (although the predicted effective activation energy was poor), but the a priori predictions were in significant error for the other systems. The Vrentas method can be used reliably for interpolation and extrapolation of limited data, although because the predicted activation energies are too low, care should be taken with extrapolation over a significant temperature range.

Keywords: MMA/PMMA system; Penetrant; Methacrylate

1. Introduction

Knowledge of diffusion coefficients of small penetrants in both rubbery and glassy polymeric matrices as a function of temperature and amount of diluent is often of considerable importance to both the experimentalist and theoretician. Major uses include modelling rates and molecular weight distributions in free-radical polymerization, and permeability studies. The availability of reliable experimental data in recent times has increased, due to the development of new techniques, and improvements in existing techniques, such as Pulsed-Field Gradient NMR [1] (PFG NMR). Although the reliability of experimental data in such systems has improved, the experiments are still complex and time-consuming. A theory that can be used reliably for quantitative prediction is clearly desirable.

One of the most popular models for diffusion of small penetrants in polymeric matrices is free volume theory. An extensive development has been given by Vrentas and Vrentas [2–9] with extensive refinements to improve the agreement between theory and available experimental data. In a recent paper, Vrentas and Vrentas [9] gave a detailed account of a means to predict most of the parameters for their treatment from physical data (experimental, or estimated from empirical correlations) for the penetrant and polymer matrix. In principle, this means it should thus be possible to *predict* diffusion coefficients of small penetrants in polymeric matrices, even for completely new systems, using only data obtained from qualitatively different sources (e.g. viscosity and density information).

In a recent study in a companion paper to the present one [10] it was shown that this parametrization of free-volume theory could not be successfully used to predict the diffusion coefficients for camphorquinone in glassy PMMA. However, use of the theory in glassy polymeric matrices is more complex than for the rubbery systems for which the model was originally developed. Furthermore, the fundamental premises of free volume theory may fail in glassy systems, where the diffusion mechanism may be qualitatively different from that assumed in the free-volume approach [10–15]. Thus it is not surprising that the predictions of the theory are not in good accord with the experimental data in such cases.

In this present paper, the predictions of free volume theory using parameters as described by Vrentas and Vrentas [9] are compared with recent PFG NMR data for monomers in rubbery PBMA and PMMA matrices over a range of monomer/polymer ratios and temperatures [16]. The primary objective is to test the validity of the method for prediction of diffusion coefficients using the parameter-estimation scheme described by Vrentas and Vrentas [9] in a

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system where reliable experimental diffusion coefficients measured over a range of matrix and penetrant type, polymer weight fraction (w_p) and temperature are available. In some cases, physical data for the estimation of some parameters were not readily available. In such cases, empirical correlations have been used to estimate the values of physical constants. The objective of the present paper is to test the a priori predictive powers of this treatment for a family of systems for which extensive data have been determined, but for which very few physical data are available. This examination of the theory is a test of how the model performs under difficult conditions.

A secondary objective of this study is to see if minimal reasonable adjustments of these calculated free volume parameters can give improved agreement between theory and experiment when limited experimental data are available, and thus to see if the free-volume treatment of Vrentas and Vrentas can be used to extrapolate and interpolate, a task which is less demanding than complete a priori prediction.

2. Free volume treatment

The free volume treatment of Vrentas and Vrentas [2–9] has undergone considerable development since its initial formulation. The central concept to free volume theory is that movement through the available free volume in the matrix governs diffusion of small penetrants in polymeric matrices. Thus, the diffusion coefficients predicted by the theory are strongly dependent on the “space-filling” properties of both the penetrant (diluent) and matrix.

The model has been shown to give good agreement with experimental data in a number of systems, when used in a correlative sense. The more recent developments to the theory have included extensions to predict all (or most) of the necessary parameters from available physical data [9]. It is this version of the theory that is used in the current study.

The basic formulation used by Vrentas and Vrentas [9] for the prediction of diffusion coefficients by free volume theory is as follows:

$$\ln D_1 = \ln \bar{D}_0 - \frac{E^*}{\mathrm{R}T} - \left\{ \frac{(1-\omega_2)\hat{V}_1^* + \xi\omega_2\hat{V}_2^*}{\hat{V}_{\mathrm{FH}}/\gamma} \right\} \tag{1}$$

where D_1 is the diffusion coefficient of the penetrant (species 1), $\bar{D}_0$ a constant, E^* the effective energy per mole that a molecule needs to overcome attractive forces, R the gas constant, T the temperature, ξ the ‘size parameter’, $\hat{V}_1^*$ and $\hat{V}_2^*$ are the specific volumes of penetrant and polymer, respectively, $\hat{V}_{\mathrm{FH}}$ the average hole free volume per unit mass of mixture, γ an average overlap value in the mixture, and $\omega_2 = w_p$.

For rubbery systems, $\hat{V}_{\mathrm{FH}}/\gamma$ can be calculated as follows:

$$V_{\mathrm{FH}}/\gamma = (1-\omega_2)\left(\frac{K_{11}}{\gamma_1}\right)(K_{21} + T - T_{g1}) + \omega_2\,\hat{V}_{\mathrm{FH2}}/\gamma_2 \tag{2}$$

where (K_{11}/γ_1) and $(K_{21} - T_{g1})$ are solvent free-volume parameters, and $\hat{V}_{\mathrm{FH2}}/\gamma_2$ is the contribution to the average hole free volume from the polymer matrix (component 2). The expression for $\hat{V}_{\mathrm{FH2}}/\gamma_2$ depends on whether the system is above or below the glass transition temperature of the matrix:

$$\hat{V}_{\mathrm{FH2}} = \hat{V}_2^0(T_{g2})[f_{\mathrm{H2}}^{\mathrm{G}} + \alpha_2(T - T_{g2})] \quad T \geq T_{g2} \tag{3a}$$

$$\hat{V}_{\mathrm{FH2}} = \hat{V}_2^0(T_{g2})[f_{\mathrm{H2}}^{\mathrm{G}} + (\alpha_2 - \alpha_{c2})(T - T_{g2})] \quad T < T_{g2} \tag{3b}$$

Here $\hat{V}_2^0(T_{g2})$ is the specific volume of the polymer at T_{g2}, $f_{\mathrm{H2}}^{\mathrm{G}}$ the fractional hole volume of the polymer at T_{g2}, α_2 the thermal expansion coefficient for the equilibrium liquid polymer, α_{c2} the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume for the equilibrium liquid polymer, T_{g2} the glass transition temperature of the pure polymer, and γ_2 the overlap factor for free volume of pure polymer. The parameters are calculated as follows:

$$f_{\mathrm{H2}}^{\mathrm{G}} = \alpha_2 K_{22}; \quad \alpha_{c2} = \frac{1}{T_{g2}} \ln\left(\frac{\hat{V}_2^0(T_{g2})(1 - f_{\mathrm{H2}}^{\mathrm{G}})}{\hat{V}_2^0(0)}\right); \qquad \gamma_2 = \frac{\hat{V}_2^0(T_{g2})\alpha_2}{(K_{12}/\gamma_2)} \tag{4}$$

$$\hat{V}_1^* = \hat{V}_1^0(0); \; \hat{V}_2^* = \hat{V}_2^0(0) \tag{5}$$

where K_{22} is one of the polymer free-volume constants, $\hat{V}_1^0(0)$ and $\hat{V}_2^0(0)$ are the specific volumes of the equilibrium liquid penetrant and polymer at $T = 0$ K, respectively, and (K_{12}/γ_2) is a polymer free-volume parameter.

The free-volume parameters K_{22} and (K_{12}/γ_2) are stated to be calculated by the expressions:

$$K_{22} = (C_2^{\mathrm{g}})_2; \; \left(\frac{K_{12}}{\gamma_2}\right) = \frac{\hat{V}_2^*}{2.303(C_1^{\mathrm{g}})_2(C_2^{\mathrm{g}})_2} \tag{6}$$

where $(C_1^{\mathrm{g}})_2$ and $(C_2^{\mathrm{g}})_2$ are WLF constants for the polymer.

The value of ξ is estimated as follows:

$$\xi = \frac{\xi_{\mathrm{L}}}{1 + \xi_{\mathrm{L}}(1 - (\bar{A}/\bar{B}))}, \; \xi_{\mathrm{L}} = \tilde{V}_1^0(0)/\tilde{V}_2^* \tag{7}$$

where $\tilde{V}_1^0(0)$ is the molar volume of the equilibrium liquid solvent (penetrant) at $T = 0$ K, $(\bar{B}/\bar{A})$ is the aspect ratio of the solvent molecule and $\tilde{V}_2^*$ the critical free volume per mole of jumping units required for a jump. E^* is estimated from the solubility parameters δ_1 and δ_2 of the penetrant and polymer using a ‘universal’ plot [9, Fig. 1], which for the present paper was fitted by:

$$\begin{aligned} &\log_{10}(E^*/\mathrm{cal\ mol^{-1}}) \\ &\quad = 0.8988 \ln\{\log(\delta_1 - \delta_2)^2\, \tilde{V}_1^0/\mathrm{cal\ mol^{-1}}\} + 2.8377 \end{aligned} \tag{8}$$

It is possible with this expression to predict meaningless values for E^* when the difference in solubility parameters is too small, due to the ln(log(x)) part of the expression.

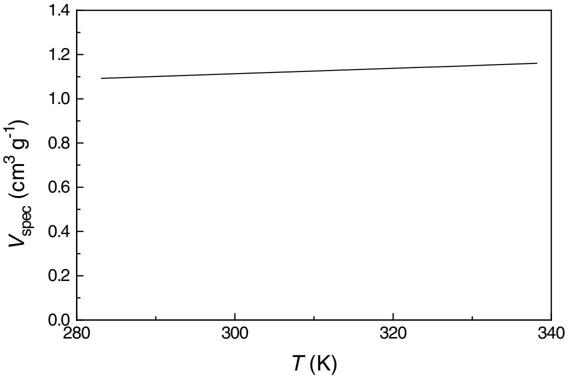

Fig. 1. Specific volume as a function of temperature for the BMA penetrant, as predicted using Eq. (13).

Undefined or negative values correspond to very small values of E^*, and are replaced by $E^* = 0$.

Methods have been given for a priori estimates of most of the parameters necessary for the above calculations in Ref. [9] These methods were used, where practical, for the estimation of the necessary parameters in the following section.

3. Estimation of parameters

The necessary parameters for the model were evaluated by the techniques given by Vrentas and Vrentas [9] Several of the parameters used in the basic formulation are derived from expressions using available physical data, as described in detail later. The derived parameters are as follows:

- $\hat{V}_1^0(0)$ (and thus $\tilde{V}_1^0(0)$) and $\hat{V}_2^0(0)$ were calculated from group contribution methods described in Ref. [17].
- $\tilde{V}_2^*$ was obtained from tabulated data, or from T_{g2}.
- f_{H2}^G was calculated from α_2 and K_{22}.
- K_{22} was calculated from the WLF constant $(C_2^g)_2$.
- (K_{12}/γ_2) was calculated from $\hat{V}_2^*$ and the WLF constants $(C_1^g)_2$ and $(C_2^g)_2$.
- γ_{c2} was calculated from $\hat{V}_2^0(T_{g2})$, α_2 and (K_{12}/γ_2).
- α_{c2} was calculated from $\hat{V}_2^0(T_{g2})$, f_{H2}^G, $\hat{V}_2^0(0)$, and T_{g2}.
- ξ_L was calculated from $\tilde{V}_1^0(0)$ and $\tilde{V}_2^*$.
- ξ was calculated from $(\bar{B}/\bar{A})$ and ξ_L.
- E^* was calculated using δ_1 and δ_2.
- $\bar{D}_0$, (K_{11}/γ_1), and $(K_{21} - T_{g1})$ were obtained from viscosity–temperature and density–temperature data.
- $\hat{V}_2^0(T_{g2})$ was calculated from density at a reference temperature and e_{pol} (the specific thermal expansivity of the polymer).
- $\hat{V}_1^0(T)$ was calculated from empirical correlations and group contribution methods described in Ref. [18] since thermal expansivity data for the penetrants were unavailable. The required raw data for the correlations were M_1 and the boiling point for the penetrant (T_b).
- $\tilde{V}_c$ was calculated from group contribution methods described in Ref. [18].

A number of the physical quantities necessary for the estimation of the free volume theory parameters are readily available from the common literature. Several other parameters can be obtained by estimation from other physical data and empirical correlations, such as found in Ref. [18] Two exceptions to the listed techniques were used:

> (a) Although in principle the aspect ratio $(\bar{B}/\bar{A})$ can be calculated using the ADAPT method [19] the software for doing this calculation is not easily implemented, and thus $(\bar{B}/\bar{A})$ was estimated by examination of space-filling models of the penetrants using Hyperchem® software.
> (b) Tabulated data for $\tilde{V}_2^*$ were not available for all systems, and an alternative estimate was made, based on a previously published correlation.

The requisite physical constants are as follows.

- Volumetric data: $\hat{V}_2^0$(298 K)(from density of the polymers at 298 K) and α_2.
- Glass transition temperatures: T_{g1} and T_{g2}.
- WLF constants: the WLF constants $(C_1^g)_2$ and $(C_2^g)_2$.
- The solubility parameters for the monomers and polymers: δ_1 and δ_2.
- The molecular weights of the penetrants: M_1.
- The boiling points of the penetrants: T_b.
- The specific thermal expansivity of the polymers: e_{pol}.
- The values of the aspect ratios $(\bar{B}/\bar{A})$ for each penetrant were crudely estimated.

Three of the necessary parameters were derived from viscosity–temperature and density–temperature data for the penetrant (solvent). The relationship between viscosity (η_1) and temperature comes from an expression by Dullien [20] and manipulated by Vrentas and Vrentas [9] to give:

$$\ln \eta_1 = \ln\left(\frac{0.124\times10^{-7}\,\tilde{V}_c^{2/3}\mathrm{R}T}{M_1\hat{V}_1^0(T)}\right) - \ln \bar{D}_0 + \frac{\hat{V}_1^*}{(K_{11}/\gamma_1)(K_{21}+T-T_{g1})} \tag{9}$$

where $\tilde{V}_c$ is the molar volume of the penetrant at its critical temperature, M_1 is the molecular weight of the penetrant, and $\hat{V}_1^0(T)$ is the specific volume of the penetrant (the inverse of the density) at the temperature of interest.

Correct choice of units is crucial in the use of this expression, and the constant 0.124×10^{-7} has been changed from the original value of 0.124×10^{-16} given in Vrentas and Vrentas [9] to reflect this. The correct units to use with this expression are η_1 in centipoise, $\tilde{V}_c$ in cm^3 mol^{-1}, M_1 in g mol^{-1}, R in J K^{-1} mol^{-1}, $\hat{V}_1^0(T)$ in cm^3 g^{-1}, $\hat{V}_1^*$ is in cm^3 g^{-1}, and the final $\bar{D}_0$ value is given in cm^2 s^{-1}. The factor of 10^9 difference arises because the original derivation of the correlation did not use SI units, resulting in an expression with a coefficient (0.124×10^{-16}) that was dependent on using the same units. The 'new' coefficient is appropriate for use with the units listed above.

A non-linear least-squares fit to Eq. (9), when used with viscosity–temperature and density–temperature relationships, gives three fitting constants, corresponding to the parameters $\bar{D}_0$ ($\mathrm{cm^2\,s^{-1}}$), (K_{11}/γ_1) ($\mathrm{cm^3\,g^{-1}\,K^{-1}}$), and $(K_{21} - T_{g1})$ (K).

In the systems tested here, the non-linear least-squares regression analysis could be reduced in complexity by linearisation of the specific volume–temperature data, which is expected to be usually accurate in a rubbery system. An example of the dependence of specific volume on temperature used in this study is shown in Fig. 1 for BMA; the method of obtaining this dependence is described in Eqs. (10)–(13) below. This dependence can be very well approximated by an expression of the form $V_{\mathrm{spec}}(T) = \hat{V}_1^0(298) + e_{\mathrm{pen}}(T - 298)$, where $V_{\mathrm{spec}}(T)$ $(= \hat{V}_1^0(T))$ is the specific volume of the penetrant at temperature T, e_{pen} is the specific thermal expansivity for the penetrant (in $\mathrm{cm^3\,g^{-1}\,K^{-1}}$), and $\hat{V}_1^0(298)$ is the specific volume of the penetrant at 298 K (this can be modified for another reference temperature if necessary). The value of e_{pen} is not the same as the value of e_{pol} (the value for the polymer, as opposed to the penetrant), and is either calculated from the literature data, or estimated from the existing or predicted specific volume–temperature data. If the experimental data used for the specific volume–temperature fitting can be approximated by a linear expansion of specific volume with temperature, the fitting is significantly simplified. The final expression to find $\bar{D}_0$, (K_{11}/γ_1) and $(K_{21} - T_{g1})$ by least-squares fitting is then:

$$\ln \eta_1 = \ln\left(\frac{0.124 \times 10^{-7}\ \tilde{V}_{\mathrm{c}}^{2/3}\mathrm{R}T}{M_1[\hat{V}_1^0(298) + e_{\mathrm{pen}}(T - 298)]}\right) - \ln \bar{D}_0 + \frac{\hat{V}_1^*}{(K_{11}/\gamma_1)(K_{21} + T - T_{g1})} \tag{10}$$

such that only one variable without a given functional form (η_1) is required; further details are given later.

For the systems tested here, neither critical volume nor viscosity–temperature data (to find $\bar{D}_0$, (K_{11}/γ_1) and $(K_{21} - T_{g1})$ using Eq. (10)) were readily available. These values were estimated as follows using empirical correlations provided in Ref. [18]

Group contribution methods and Eq. (11) were used to estimate the critical volume:

$$\tilde{V}_{\mathrm{c}} = 33.04 + \left(\sum_i (M_i\ \Delta V_i)\right)^{1.029} \tag{11}$$

where M_i and ΔV_i are the mass and volume contributions from each group, respectively. The group volume contributions are tabulated in Ref. [18] The average error in the predicted values from use of this correlation is approximately 1%, up to a maximum of 6% for complex liquids.

The viscosity–temperature data were estimated using a very crude correlation based on the density of the penetrant [21]:

$$\log_{10}(\log_{10}(10 \times \eta_1)) = \frac{I}{M_1}\rho - 2.9 \tag{12}$$

where I is Souders' index, which is determined from group contributions given in Ref. [21] and ρ is the density ($\mathrm{g\,cm^{-3}}$). Typical errors from the use of this expression are of the order of 10%. Since insufficient density–temperature data are available for the present systems, the specific viscosity–temperature data were estimated by use of an empirical correlation quoted by Perry: [18]

$$\ln (V_{\mathrm{sat}}P_{\mathrm{c}}/\mathrm{R}T_{\mathrm{c}}) = (\ln U)^0 + \omega(\ln U)^1 \tag{13}$$

where V_{sat} ($\mathrm{cm^3\,mol^{-1}}$) is the saturated-liquid molar volume, P_{c} is the critical pressure, ω the acentric factor, and $(\ln U)^0$ and $(\ln U)^1$ are functions of the reduced temperature ($T_{\mathrm{r}} = T/T_{\mathrm{c}}$) [18]:

$$\begin{aligned}(\ln U)^0 = {} & \ln T_{\mathrm{r}} + 1.39644 - 24.076\,T_{\mathrm{r}} + 102.615\,T_{\mathrm{r}}^2 \\ & - 255.719 T_{\mathrm{r}}^3 + 355.805\,T_{\mathrm{r}}^4 - 256671\,T_{\mathrm{r}}^5 \\ & + 75.1088\,T_{\mathrm{r}}^6\end{aligned} \tag{14a}$$

$$\begin{aligned}(\ln U)^1 = {} & 13.4412 - 135.7437\,T_{\mathrm{r}} + 533.380\,T_{\mathrm{r}}^2 \\ & - 1091.453\,T_{\mathrm{r}}^3 + 1231.43\,T_{\mathrm{r}}^4 - 728.227\,T_{\mathrm{r}}^5 \\ & + 176.737\,T_{\mathrm{r}}^6\end{aligned} \tag{14b}$$

This expression normally yields errors of less than 1% for non-polar compounds. The specific volume at each temperature can then be calculated by dividing V_{sat} by the molar mass of the penetrant. The density is the reciprocal of the specific volume.

The procedure used here for the fitting of Eq. (10) was to first generate the specific-volume/temperature data using the cited empirical correlation (Eq. (13)), which then gives ρ, then the viscosity–temperature data using Eq. (12), followed by fitting of the resultant curve by non-linear regression (least-squares residual minimisation) to Eq. (10) to find $\bar{D}_0$, (K_{11}/γ_1) and $(K_{21} - T_{g1})$. The uncertainties in the three fitted parameters were estimated by the standard errors in those parameters, and were generally quite small with respect to their corresponding parameters. However, the apparently small uncertainties are deceptive, since the data used to generate the specific volume and viscosity data are of very dubious quality, and would result in far larger errors than given by the calculated uncertainties from the regression step. An example of this problem is the use of empirical correlations for the estimation of the specific-volume/temperature data, described in further detail after Eq. (12); this involves numerous estimations, each of which may result in significant error. No simple means of

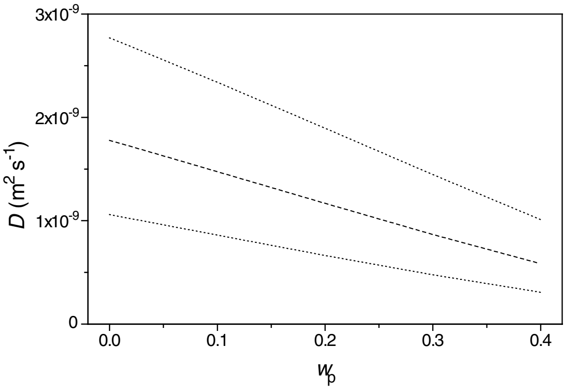

Fig. 2. Sensitivity of the predicted diffusion coefficients to the output parameters from the non-linear regression step for MMA in PMMA at 298 K. The dashed line corresponds to the diffusion coefficients predicted by the best fit parameters, and the extreme (dotted) lines to the diffusion coefficients predicted by setting all output parameters to the values at either extreme of the 95% confidence range for each parameter.

estimating the real uncertainties and errors is available for such a system.

The sensitivity of the predicted diffusion coefficients to uncertainties in the output parameters from the fitting step gives an indication of the potential errors introduced in that step. This estimate neglects uncertainties from other sources of error, and should only be used as a guide to the potential errors introduced from the fitting procedure. A comparison of the predicted diffusion coefficients generated at 298 K for MMA, using the best estimated parameters generated in this section, and data generated with all fitting parameters at either extreme of the 95% confidence range, are shown in Fig. 2. Note that the two extreme curves actually *overestimate* the potential errors introduced in the fitting step, since all three output parameters are at their extreme values in these cases, a situation that lies significantly outside the 95% *joint* confidence range.

The critical temperatures were estimated by an empirical correlation using group contribution methods [18]:

$$T_c = \frac{T_b}{0.567 + \Sigma_{\Delta_T} + (\Sigma_{\Delta_T})^2} \tag{15}$$

where the temperatures are in K, T_b is the boiling point of the penetrant, and the Δ_T values are temperature contributions from each group as listed in Ref. [18]. Errors in T_c when estimated by this method are usually less than 2%.

The critical pressures were estimated by an empirical correlation using group contribution methods [18]:

$$P_c = \frac{M_1}{(0.34 + \Sigma\Delta_p)^2} \tag{16}$$

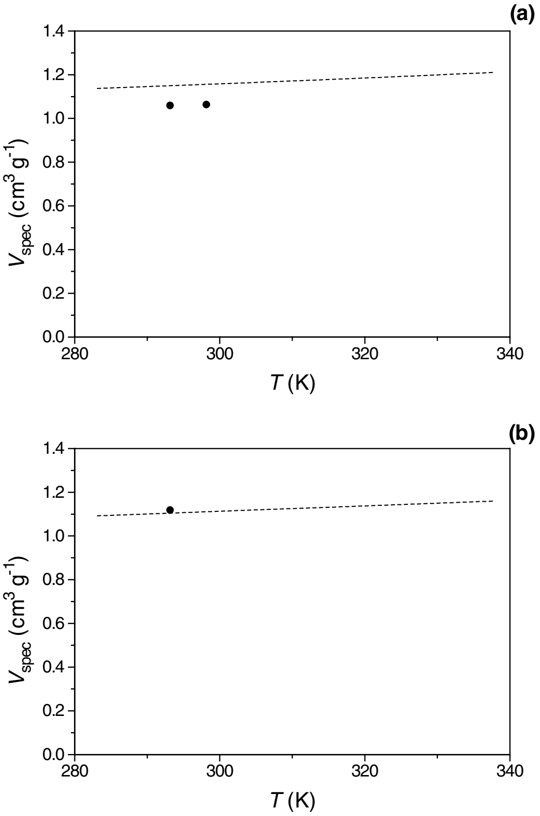

Fig. 3. Specific volume versus temperature for (a) MMA and (b) BMA, as predicted (unbroken lines) by Eq. (13). Experimental data points from the literature [22] are shown for comparison (points).

where the Δ_p values are pressure contributions from each group as listed in Ref. [18] and P_c is in atmospheres. Critical pressures calculated using this expression usually yield errors of less than 5%.

The acentric factors were estimated by an empirical correlation using group contribution methods [18]:

$$\omega = \frac{-\ln P_c - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.169347\ \theta^6}{15.2518 - 15.6875\ \theta^{-1} - 13.4721 \ln \theta + 0.43577\ \theta^6} \tag{17}$$

where $\theta = T_b/T_c$.

The errors introduced by use of such correlations can be significant, especially in this case where the errors introduced by several correlations are likely to compound. In the case of both BMA and MMA, some density data are available for comparison [22]. Specific volume-temperature data (based on the empirical correlations) for the two penetrants are shown in Fig. 3, with available literature data points shown for comparison. It can be observed that the data are quite close to linear for both systems (although there is a slight deviation from linearity in the case of MMA that is not observable on the scale of the figure). A linear fit of the data for MMA gives a thermal expansion coefficient of 1.34×10^{-3} cm^3 g^{-1} K^{-1}. The estimate of the

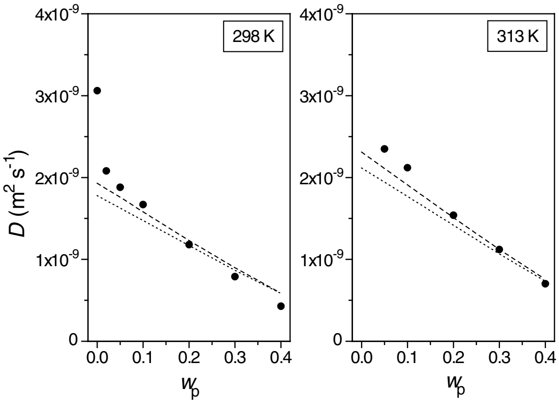

Fig. 4. Predicted effect (dashed line) of the discrepancy in specific volume for MMA, generated by using different output parameters from the non-linear regression fit to alternative specific-volume/temperature data for MMA (from the semi-empirical correlation method, dotted line, and using the thermal expansion coefficient from the data of Fig. 3, broken line). Experimental diffusion coefficients (points) are shown for comparison.

Table 1
Raw data for the calculation of the free volume parameters used for the prediction of diffusion coefficients for BMA and MMA in PBMA and rubbery PMMA

Parameter	BMA or PBMA	MMA or PMMA
M_1 (g mol^{-1})	142.2	100.12
T_{g2} (K) [22]	293	388
$\hat{V}_2^0$ (298 K) (cm^{3}g^{-1}) [22]	0.9497	0.8547
α_2 (K^{-1}) [22]	6.10×10^{-4}	5.70×10^{-4}
$(C_1^g)_2$ (dimensionless) [22]	9.7	32.2
$(C_2^g)_2$ (K) [22]	169.6	80
δ_1 (J$^{1/2}$ cm$^{-3/2}$) [22]	16.8	18.0
δ_2 (J$^{1/2}$cm$^{-3/2}$) [27]	18.1	18.6
T_b (K) [22]	434	373
e_{pol} (cm^3 g^{-1} K^{-1}) [27]	5.35×10^{-4}	6.10×10^{-4}
$(\bar{B}/\bar{A})$ (dimensionless)	1.9	1.2
$\hat{V}_1^0$(293 K) (cm^3 g^{-1}) [22]	1.119	1.068

thermal expansion coefficient from the above empirical-correlation method is significantly smaller: 9×10^{-4} cm^3 g^{-1} K^{-1}. The predicted value of the density at 298 K is also significantly different for this system: 0.870 g cm^{-3} from the correlation, and 0.940 g cm^{-3} from the literature data. For MMA, the experimental specific volume points deviate significantly from the prediction. The prediction for BMA appears to be quite good at the one temperature where existing data are available for comparison. The effect of the discrepancy in the specific volume data for MMA is to generate quite different values of $\bar{D}_0$, (K_{11}/γ_1) and $(K_{21} - T_{g1})$ from the non-linear regression.

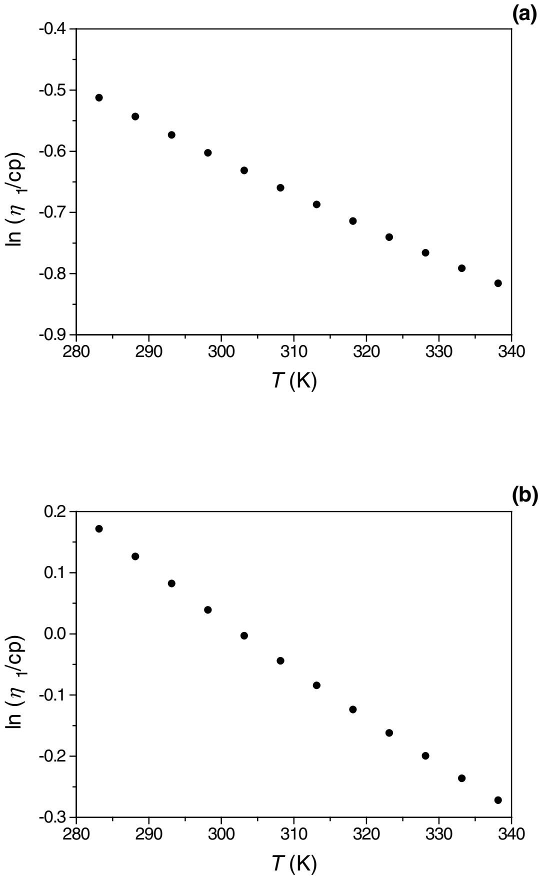

Fig. 5. Viscosity–temperature relation for (a) MMA and (b) BMA, as predicted by Eq. (12).

Fortunately, the different values of $\bar{D}_0$ (K_{11}/γ_1) and $(K_{21} - T_{g1})$ do not produce significantly different predicted diffusion coefficients at either temperature, as shown in Fig. 4, although there is a slight effect on the w_p-dependence. The viscosity–temperature dependences for the two monomers calculated using the above treatment used to obtain these parameters are shown in Fig. 5. These data were generated by Eq. (12), using the specific volume (or density) data predicted using Eq. (13). The fit to these dependences with Eq. (10) is indistinguishable from the input curve, which is not surprising with three fitting parameters.

Use of Eq. (12) to predict viscosity–temperature data may introduce some problems, due to both the relatively high errors, and the forced correlation between the viscosity and density data, which is then used in the regression step. The forced correlation between density and viscosity may also cause the resulting viscosity–temperature plot to be less steep than expected, due to the assumed linearity of the volumetric behaviour with temperature. This may have an effect on the “curvature” term $(K_{21} - T_{g1})$ resulting from the fitting process, which will in turn affect the curvature of both the temperature and w_p dependences of the diffusion coefficients predicted by Eq. (1).

The parameter $\tilde{V}_2^*$ is sometimes [9] available in tabulated data. The appropriate value for PMMA is found in Table 4 of the above reference. However, no value for PBMA is available. Thus, this parameter was estimated as described by Zielinski and Duda [23] from T_{g2} (note the units in

Table 2
Calculated free volume parameters used for the prediction of diffusion coefficients of MMA and BMA in PBMA and rubbery PMMA

Parameter	BMA or PBMA	MMA or PMMA
$\hat{V}_1^0(0)$ $(= \hat{V}_1^*)$ (cm^3 g^{-1})	0.771	0.871
$\tilde{V}_1^0(0)$ (cm^3 mol^{-1})	130.4	86.9
$\hat{V}_2^0(0)(= \hat{V}_2^*)$ (cm^3 g^{-1})	0.788	0.762
$\tilde{V}_2^*$ (cm^3 mol^{-1})	85.4	135
f_{H2}^G (dimensionless)	0.103	0.00456
K_{22} (K)	169.6	80
(K_{12}/γ_2) (cm^3 g^{-1} K^{-1})	2.08×10^{-4}	1.28×10^{-4}
γ_2 (dimensionless)	2.79	3.88
α_{c2} (K^{-1})	8.23×10^{-4}	2.37×10^{-4}
ξ_L (dimensionless)	1.53	0.64 in PMMA 0.91 in PBMA
ξ (dimensionless)	0.89	0.58 in PMMA 0.79 in PBMA
E^* (J mol^{-1})	8927	2127 in PMMA 0 in PBMA
$\bar{D}_0$ (cm^2 s^{-1})	8.68×10^{-4}	1.27×10^{-3}
(K_{11}/γ_1) (cm^3 g^{-1} K^{-1})	9.42×10^{-4}	6.91×10^{-4}
$(K_{21} - T_{g1})$ (K)	−82.41	72.26
$\hat{V}_2^0(T_{g2})$ (cm^3 g^{-1})	0.9497	0.8754
$\tilde{V}_c$ (cm^3 mol^{-1})	458	311

this relation):

$$\tilde{V}_2^*(\mathrm{cm^3\ g^{-1}}) = 0.6224\ T_{g2}(\mathrm{K}) - 86.95 \tag{18}$$

Although Vrentas et al. [8] later described this empirical correlation as giving poor agreement with fitted data for some systems, no other estimates were available, and thus this correlation was chosen by default.

The raw data that were used to calculate the necessary parameters for each system are shown in Table 1, and the derived quantities used in the calculations in Table 2.

4. Comparison with experimental diffusion coefficients

The experimental data of Griffiths et al. [16] are for BMA and MMA oligomers in rubbery PBMA and PMMA matrices over a range of weight-fraction polymer and of temperature. The data of interest here are the diffusion coefficients of the monomeric species in those matrices. The combinations studied were MMA in PMMA, MMA in PBMA, and BMA in PBMA. In most systems only a small amount of the monomer was present, with the remainder of the "solvent" component (the diluent) being the saturated analogues of the monomers: butyl isobutyrate in the case of BMA, and methyl isobutyrate in the case of MMA. In these cases, although the systems were truly ternary, it has been assumed that the diluent has the same properties as the penetrant, which allows the ternary systems to be treated as the simpler analogous binary systems. This is probably a reasonable approximation, since these analogues have similar structure, functionality, molecular size, and molecular weight as their respective monomers.

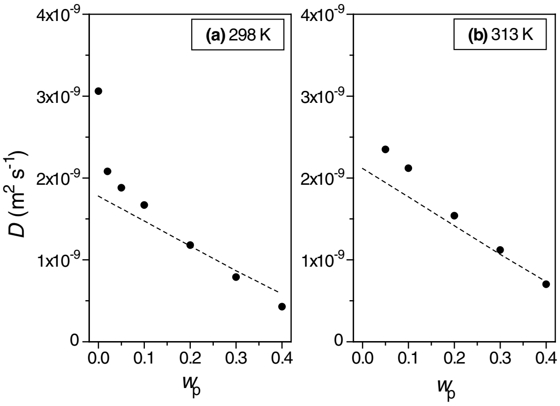

Fig. 6. Predicted (dashed line, as obtained with the completely a priori treatment) and the observed diffusion coefficients for MMA in PMMA: (a) at 298 K; (b) at 313 K.

The experimental data were for a range of w_p values in the rubbery regimes, and two temperatures 298 and 313 K. All measured diffusion coefficients were averages over several readings, and should be regarded as of both high accuracy and precision. It is important to note that the data show a qualitative change in diffusion coefficients as the polymer weight fraction goes from effectively infinite dilution to values of a few percent. This may possibly be an experimental artefact due to thermal diffusion effects [24] or, as discussed by Griffiths et al. this probably corresponds to c^* (where polymer chains start to overlap). It is possible that the diffusion mechanism is different above and below c^*, and that the free volume mechanism is only valid when chains overlap, i.e. above c^*.

Figs. 6–8 show the comparison between the experimental diffusion coefficients and those predicted from the free-volume formulation of Vrentas and Vrentas [9] using the parameter set described in the previous section. While the accord with MMA in PMMA is good, it is only moderate for MMA in PBMA, and very poor for BMA in PBMA.

The sensitivities of the predicted diffusion coefficients for each system and temperature to uncertainties in the output parameters from the non-linear regression step are shown in Fig. 9, and to the aspect ratios are shown in Fig. 10. The experimental data are shown for comparison in each case.

The extreme curves on the plots of the sensitivities to the output parameters from the non-linear regression step are again taken with all output parameters set at the extreme ends of the 95% uncertainty regions for each parameter. As previously stated, this is likely to overestimate the uncertainties from these sources. The extreme curves in the sensitivity plots for the aspect ratios of the penetrants are also for cases where the input parameters used to generate these curves are outside the reasonable ranges estimated for the uncertainty limits. The values chosen for the ranges of the aspect ratios (based on examination of the molecular models for the penetrants) are for MMA: 1–1.4 (best estimate: 1.2); and for BMA: 1.3–2.5 (best estimate: 1.9).

It is clear from these figures that reasonable uncertainties in these parameters for both sets of parameters cannot

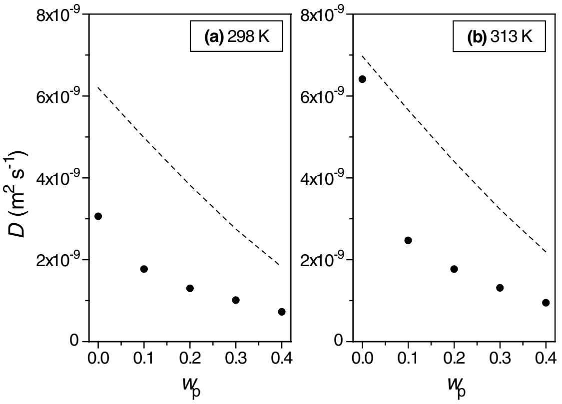

Fig. 7. Predicted (dashed line, as-obtained with the completely a priori treatment) and observed diffusion coefficients for MMA in PBMA: (a) at 298 K; (b) at 313 K.

account for the discrepancies between the predicted diffusion coefficients (and their w_p-dependence) and the experimental values for the PBMA systems.

In the case of the MMA in PMMA (Fig. 6), the agreement between theory and experiment is fairly good at 298 K, with a larger deviation at 313 K. The only large apparent discrepancy is at very low w_p (here at $w_p = 0$), which is to be expected for all of the systems studied here, and corresponds to the apparent anomaly observed in the experimental diffusion coefficients at very low w_p [16]. Note that although in both cases the absolute values closely correspond, the slopes of the variation with w_p are significantly different. This system is probably the best studied of the systems examined here, and thus is most likely to have accurate raw data for the estimation of the parameters used in the prediction of the diffusion coefficients.

This system has been previously examined with simpler, and less a priori, formulations of the Vrentas free volume model. Griffiths et al. [16] used the model in the correlative sense to generate best-fit parameters for their data, based on modified parameters derived from fits to previous data by Faldi et al. [25] and Waggoner et al. [26] A comparison of the parameters is shown in Table 3, and the predicted diffusion coefficients at 298 K in Fig. 11. The parameter set used in Griffiths et al. provided a quite good fit to the experimental data, and there are small but significant differences between the predicted diffusion coefficients using the

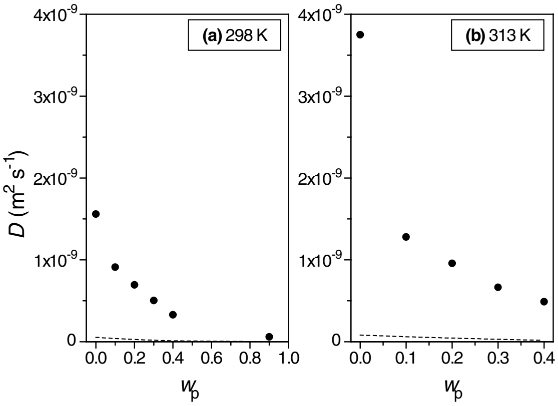

Fig. 8. Predicted (dashed line, as-obtained with the completely a priori treatment) and observed diffusion coefficients for BMA in PBMA: (a) at 298 K; (b) at 313 K.

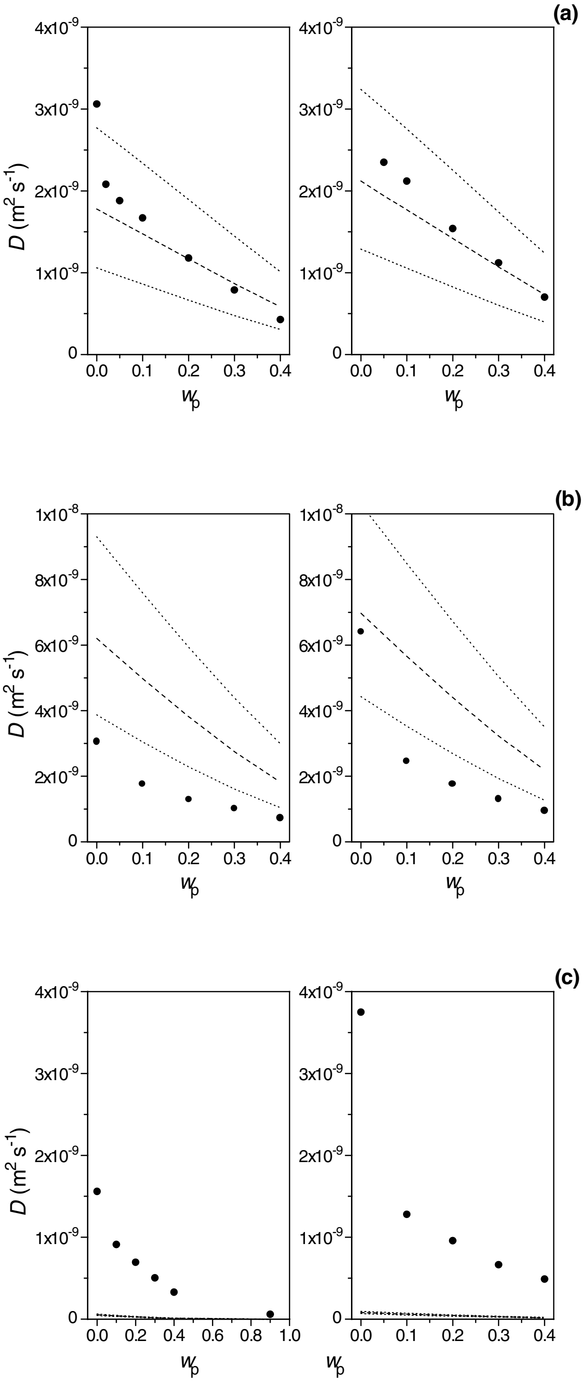

Fig. 9. Sensitivity of the predicted diffusion coefficients for each system to the output parameters from the non-linear regression step: (a) MMA in PMMA; (b) MMA in PBMA; (c) BMA in PBMA. The dashed lines correspond to the diffusion coefficients predicted by the best fit parameters, and the extreme (dotted) lines to the diffusion coefficients predicted by setting all output parameters to the values at either extreme of the 95% confidence range for each parameter.

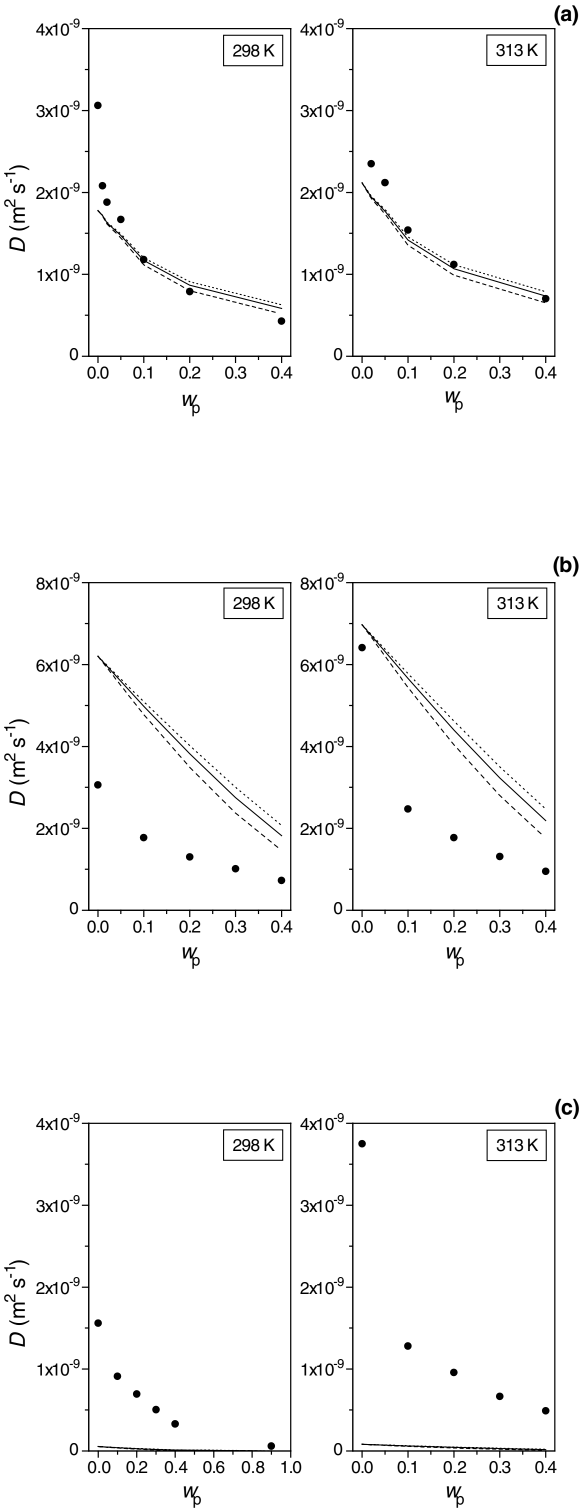

Fig. 10. Sensitivity of the predicted diffusion coefficients to the aspect ratio ($\bar{B}/\bar{A}$) values used in the calculations, at each temperature: (a) MMA in PMMA; (b) MMA in PBMA; (c) BMA in PBMA. The unbroken lines correspond to the diffusion coefficients predicted by the best-fit parameters, the dashed lines to those predicted at the low end of the ($\bar{B}/\bar{A}$) range, and the dotted lines to those predicted at the high end of the ($\bar{B}/\bar{A}$) range. The ($\bar{B}/\bar{A}$) values used were: MMA — low = 1, best = 1.2, high = 1.4; BMA — low = 1.3, best = 1.9, high = 2.5.

present totally a priori parameter set. This is not surprising, since the parameters in the study of Griffiths et al. were adjusted so as to provide a good fit to the experimental data, whereas the current parameter set are predicted in an a priori sense from physical data.

The case of MMA diffusing in PBMA poses a more stringent test. Most of the parameters for the MMA penetrant can be directly transferred from the MMA in PMMA system, since a number of these parameters are predicted to be intrinsic to the monomer, rather than to the system as a whole. Since the fit to the MMA in PMMA data is relatively good, it would be expected that the parameter set for MMA in PBMA would predict diffusion coefficients in good agreement with experiment. However, the observed differences (Fig. 7) between the predicted and the experimental data are significant, both in terms of absolute values and slope.

It was found that the agreement between the a priori theory and experiment in this system is not particularly good, with the data differing by a factor of about 2–3 throughout the range tested, at both temperatures. This is despite a number of the parameters being the same as the MMA in PMMA system, where the agreement between theory and experiment is good. Now, there are a number of parameters for which there is considerable uncertainty, including the parameter $\tilde{V}_2^*$ for the PBMA matrix, for which no good parameter estimate scheme could be found. However, the sensitivity analyses show that reasonable variations in most of these parameters cannot account for the observed discrepancies, with the exception being the value of E^*, which has a significant effect on the absolute values of the predicted diffusion coefficients. The uncertainty in the value of $\bar{D}_0$ is expected to be small, but since the fitting was based on predicted data, the errors may be larger than otherwise expected. Changing the value of $\bar{D}_0$ will have a significant effect on the absolute values of the diffusion coefficients at both temperatures, but not on the w_p-dependence. Now, the discrepancies here are not only in the absolute values of the diffusion coefficients, but also in the w_p-dependence. Thus, allowing for uncertainties in the value of $\bar{D}_0$ is not sufficient to explain the observed discrepancies.

Increasing the value of E^* to approximately 2 kJ mol^{-1} in this system dramatically improves the agreement between theory and experiment, although the slope with respect to w_p is still in poor agreement (see Fig. 12). Such a difference in predicted values of E^* is certainly reasonable, since the values of the solubility parameters for the penetrant and matrix are usually quoted as fairly broad ranges in the literature. However, the value of the solubility parameter used in this calculation of E^* for the MMA penetrant is the same as that used in the calculations for MMA in PMMA, which gives good agreement with experiment in that case. Thus, changing the value of the solubility parameter for MMA in this case is not internally consistent: good agreement for both systems cannot be reached simultaneously. Furthermore, the primary objective of this study is to see if a priori

Table 3
Comparison of predicted free volume theory parameters with those of Griffiths et al. [16] (*) This term was incorporated into the term ($K_{22} - T_{g2}$) in the earlier version of the theory used in Griffiths et al.

Parameter	Current study	Based on Faldi [25]	Based on Waggoner [26]
E^* (J mol^{-1})	2127	3255	0
$\hat{V}_1^*$ (cm^3 g^{-1})	0.871	0.87	0.771
$\hat{V}_2^*$ (cm^3 g^{-1})	0.762	0.757	0.788
ξ (unitless)	0.644	0.60	0.92
T_{g2} (K)	388	392	392
K_{22}/ (K (*))	80	52.4	91
$\bar{D}_0$ (cm^2 s^{-1})	1.27×10^{-3}	2.74×10^{-3} (adjusted to 1.61×10^{-3} in Ref. [16])	9×10^{-5}
(K_{12}/γ_2) (cm^3 g^{-1} K^{-1})	1.28×10^{-4}	4.77×10^{-4}	3.05×10^{-3}
(K_{11}/γ_1) (cm^3 g^{-1} K^{-1})	6.91×10^{-4}	8.15×10^{-4}	1.17×10^{-3}
($K_{21} - T_{g1}$) (K)	72.26	0	−51.37

estimates of the parameters will give good agreement with experiment, since this is exactly the case that may be faced when working with a system for which there are no experimental data. Only in the case where limited experimental data are available can one make changes in the model parameters to improve agreement between theory and experiment. In this case, given one experimental data point (above c^*), the experimental data can be reasonably well predicted across the entire range by adjusting one parameter, E^*.

The final system considered here was BMA penetrant in PBMA matrix. In this case, there are no parameters available for guidance or comparison. That is, for the purposes of this study, this is a completely new system. As can be seen in Fig. 8, the agreement between theory and experiment is very poor at both temperatures, differing by more than an order of magnitude in all cases, up to approximately 4 orders of magnitude at high w_p (where the system is still rubbery). The major reasons for the discrepancy in this case appear to be in the relatively high predicted value of E^* (approximately 9 kJ mol^{-1}), and a poor estimation of the w_p dependence, which is most apparent at $w_p = 0.9$. The actual activation energy, E_a, which of course is different from E^*, is found from numerical differentiation of an Arrhenius plot: $E_a = R\partial(\ln D)/\partial(-1/T)$ (these plots generated by Eq. (1) are slightly curved but the temperature dependence of E_a so obtained is negligible). The predicted E_a is approximately 23.1 kJ mol^{-1}, compared with the experimental estimate of 17.5 kJ mol^{-1}.

The high value of E^* is the major cause of the discrepancies, and reduction of E^* to zero provides a fairly good fit at the low w_p end. However, the large drop in experimental diffusion coefficients at $w_p = 0.9$ cannot be predicted using this modification of the parameter set. Thus, the anomalous value of E^* is not the only problem for this system. This is the only system which is rubbery over a wide range of w_p, and thus where the diffusion coefficients can be compared over such a wide range of w_p values. The poor accord suggests that the w_p dependence of the diffusion coefficients cannot be predicted using this parameter evaluation scheme in the general case. Note also that although this system is the furthest from those previously studied (of the three systems studied here), the parameter evaluation scheme was the same in each case, so the lack of previous data had no effect on the results. It is, however possible, that the input data (density etc.) used to estimate the free volume parameters were not of the same reliability as for the well-studied

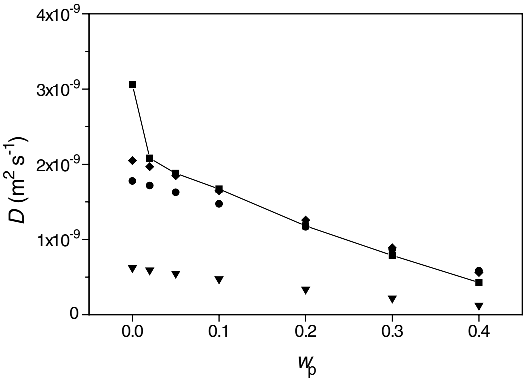

Fig. 11. Comparison of predicted data in current study for MMA in PMMA with those predicted using the parameter set of Griffiths et al. [16] at 298 K. Circles: diffusion coefficients predicted with the current model and parameters; diamonds: using the parameters of Faldi et al. [25] triangles: using the parameters of Waggoner et al. [26] The unbroken line links experimental data points for comparison.

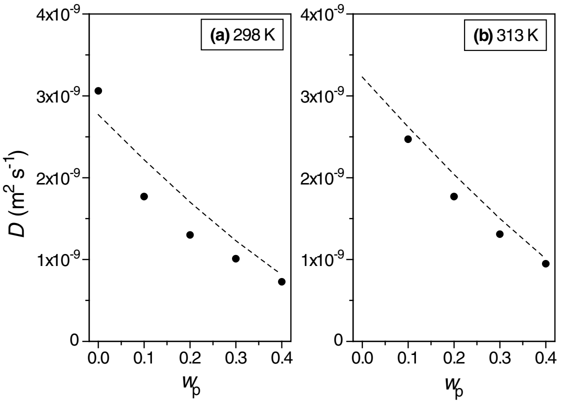

Fig. 12. Predicted (dashed lines) and observed diffusion coefficients (individual points) for MMA in PBMA, using $E^* = 2$ kJ mol^{-1} : (a) at 298 K; (b) at 313 K.

MMA/PMMA combination. This may explain why the discrepancies were largest for this system, but this system was also the most critical test of the parameter evaluation scheme. Thus, it would appear that the scheme cannot always be used reliably to predict diffusion coefficients (and activation energies for diffusion) for completely new systems, especially over a wide w_p range.

A final scenario was considered for each of the systems: given diffusion coefficients for the penetrants at two temperatures at the same w_p, would it then be possible to improve the agreement between theory and experiment by using the temperature dependence of the experimental data to modify the predicted value of E^*? Experimental diffusion coefficients at two temperatures under the same conditions allow a crude estimate of the activation energy for the penetrant diffusion in the system. The free volume expression for the diffusion coefficients in Eq. (1) can be broken into two temperature-dependent and temperature-independent components. The temperature-dependent part can be further divided into two independent parts: the E^* term, and the free volume term. The activation energy can be considered to be the sum of two parts: $E_a = E^* + E_2$, where the term E_2 contains the temperature dependence of the free volume contributions. Thus, by adjusting the value of E^*, it would be possible to set the effective activation energies to be equivalent (i.e. $E_{a,\text{experiment}} = E_{a,\text{predicted}}$) at that particular value of w_p. This might improve the agreement between theory and experiment for the predicted diffusion coefficients.

This strategy was attempted at $w_p = 0.1$ for all three systems, and it was found that this approach generally did not improve the agreement between experiment and theory. In fact, in the case of MMA diffusion in PBMA, this approach predicted an E^* value of approximately 10 kJ mol^{-1} whereas the a priori prediction was approximately 0 kJ mol^{-1}. It was earlier established that, at a single temperature, an E^* value of approximately 2 kJ mol^{-1} was more appropriate. The most likely reasons for this discrepancy are as follows: poor estimates of the experimental activation energies (use of only two points, plus experimental uncertainties) and errors in either the theory or the free volume terms (quite possible). Note that this discrepancy also highlights the fact that the predicted activation energies are also normally quite poor, even when the absolute agreement between theory and experiment are reasonably good over a limited temperature range, as in the case of MMA diffusing in PMMA. In that case, the experimental and predicted values of E_a are ~12 and ~9 kJ mol^{-1}, respectively. Thus a significant change in E^* would be necessary to compensate for this, which would increase the discrepancies between theory and experiment if extrapolated to a wider temperature range.

This suggests that some of the sources of the discrepancies might be in the free volume terms. This is also implied in Fig. 6, where the curves cross at 298 K at $w_p = 0.2$, but cross at $w_p = 0.35$ at 313 K.

5. Discussion

Several of the discrepancies between the predicted and experimental diffusion coefficients may be attributed to the sometimes large uncertainties in the raw experimental data (or poor correlations) used in the parameter estimation schemes. The prediction of some of the free volume parameters is highly sensitive to the input data.

The prediction of E^* is an important example of this situation. The literature data for the solubility parameters for the penetrants and polymers are given as a range, which is sometimes quite broad. The functional form for the dependence of E^* on these data is very sensitive to deviations in these parameters, which can result in large differences in the predicted values of E^*. Furthermore, the fitting step to produce the correlation used does not fit all of the original data, and some points deviated significantly from the curve. This suggests that the correlation is only very approximate, and may fail quite badly for some systems. This point is particularly important for the prediction of diffusion coefficients, since the model is very sensitive to the value of E^*, and this quantity makes a large difference to both the absolute values of the diffusion coefficients of the penetrants and to their predicted temperature dependence.

Another area where significant errors may be generated is in the non-linear regression step to evaluate $\bar{D}_0$, (K_{11}/γ_1), and $(K_{21} - T_{g1})$. Since the fitting is to a correlation of more than one parameter-temperature data set, uncertainties in any of the parameter sets may lead to large errors in the final output parameters. $\bar{D}_0$ and (K_{11}/γ_1) particularly have a significant effect on the predicted diffusion coefficients. The parameter $\bar{D}_0$ affects the absolute values of the predicted diffusion coefficients at all temperatures and compositions. The parameter (K_{11}/γ_1) has a strong effect on the curvature of the predicted plots of the diffusion coefficients versus w_p, and may be responsible for the common failure to predict their dependence on sample composition. Overall, the best predictions are a result of reliable input data. It is recommended that correlations of the type used here be used only where necessary, and that the user be aware of the potential for significant errors in this step.

As stated, reasonable estimates of the uncertainties in the values of these three fitted parameters cannot bring about good accord with experiment for the BMA system. Errors in the estimation of other parameters, such as the aspect ratio, and uncertainties in the output parameters resulting from the fitting of the viscosity–temperature data, were found to be relatively small. The observed discrepancies between predicted and observed diffusion coefficients could not be attributed to these sources for the systems examined. Thus, these areas should be considered minor sources of error compared with those described above.

6. Conclusions

The predictions of free volume theory using the parameter estimation scheme of Vrentas and Vrentas were tested for several systems. The predictions were made with limited physical data and empirical correlations, and could be considered a worst-case examination of the predictive power of the theory and parameter examination scheme.

Use of the parameter estimation scheme of Vrentas and Vrentas is likely to work best in combination with limited experimental data, where the possibility for correction of the parameters may exist by comparison of prediction with experiment. The two most readily adjustable parameters, for which there may be considerable uncertainty, are $\bar{D}_0$ and E^*. At a single temperature, changing either of these has the effect of shifting the entire predicted curve. However, changing the value of E^* will change the temperature dependence of the predicted data, so this approach should be used more carefully, and is best used when the value of E^* is obviously incorrect, there exist experimental data which suggest this change, or other changes would not be reasonable.

The predicted diffusion coefficients using the parameter estimation scheme of Vrentas and Vrentas were generally in poor agreement with the corresponding experimental data of Griffiths et al. The exception was the MMA diffusing in PMMA, where the agreement of the absolute values of the diffusion coefficients for the two data sets was fairly good, but the agreements for the temperature and w_p dependences were not. The absolute values of the predicted diffusion coefficients for the other systems examined here were always rather poor. This was particularly the case for BMA diffusing in PBMA, for which there were no previously existing data. The problem was exacerbated in this system by the problem of parameter generation, where $\tilde{V}_2^*$ is not available in tabulated data. This system highlights the problem of predicting diffusion coefficients over a wide range of w_p values, where the w_p dependence is often poorly predicted, and thus large deviations between theory and experiment are possible.

The agreement between the predicted and experimental data could be improved in some cases by limited adjustment of the predicted parameters, with the assistance of limited experimental data. This could in some cases improve the agreement in the absolute values of the diffusion coefficients or temperature dependences, but not the w_p dependences. Certainly the agreement could be improved by adjusting a large number of parameters, but the objective of this study was to test the predictive power of the parameter estimation scheme of Vrentas and Vrentas with limited or no experimental data.

It must be admitted that some of the procedures used to obtain the free-volume parameters are of a quality that is unable to provide a true test of the adequacy of the Vrentas treatment to provide a reliable a priori fit: for example, the density/viscosity data correlation and the crude method for estimating the aspect ratio could certainly be improved if better data were available. However, the procedures used here test the usefulness of the approach for *practical* application: for example, the effort required to obtain better viscosity and density data for these common monomers is about the same as that required to measure the diffusion coefficients themselves!

The overall usefulness of the parameter estimation scheme and theory depends on the overall expectations of the user, and the amount of existing experimental data. In some cases, the model predicts diffusion coefficients that are within a factor of two of the experimental quantities, which may be acceptable in some cases. However, for other systems, the discrepancies are up to several orders of magnitude, which is rarely likely to be considered acceptable. The agreement between experiment and theory in these cases may sometimes be improved with the assistance of limited experimental data. The ability of the parameter estimation scheme to predict experimental data over a wide range of temperature and w_p appears to be generally poor, which restricts the utility of the scheme to limited ranges of these quantities. If highly accurate predictions over a wide range of conditions is desired, the scheme is unlikely to be sufficient; however, if approximate diffusion coefficients in a narrow range of conditions are desired, acceptable predictions may be made in some cases, especially if there exist some corresponding experimental data.

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