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Determination of Free-Volume Parameters for Solvent Self-Diffusion in Polymer−Solvent Systems

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Introduction

In two recent papers,[1,2] a free-volume theory of transport was developed for predicting and correlating solvent self-diffusion coefficients for both rubbery and glassy polymer−solvent systems. For a rubbery polymer−solvent system, it was shown that concentration and temperature variations of the solvent self-diffusion coefficient, D_1, can be determined using the following equations:[1]

$$D_1 = \bar{D}_0 \exp\left[-\frac{E^*}{RT}\right] \exp\left[-\frac{\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*}{\hat{V}_{FH}/\gamma}\right] \tag{1}$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1}(K_{21} + T - T_{g1}) + \frac{\omega_2 \hat{V}_{FH2}}{\gamma_2} \tag{2}$$

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

$$\hat{V}_{FH2} = \hat{V}_2^0(T_{g2})\left[f_{H2}^G - \int_T^{T_{g2}} (\alpha_2 - \alpha_{C2})\, dT'\right] \qquad T < T_{g2} \tag{4}$$

$$\alpha_{C2} = \frac{\ln\left[\dfrac{\hat{V}_2^0(T_{g2})(1 - f_{H2}^G)}{\hat{V}_2^0(0)}\right]}{T_{g2}} \tag{5}$$

$$f_{H2}^G = \alpha_2 K_{22} \tag{6}$$

$$\gamma_2 = \frac{\hat{V}_2^0(T_{g2})\alpha_2}{K_{12}/\gamma_2} \tag{7}$$

$$\hat{V}_1^* = \hat{V}_1^0(0) \tag{8}$$

$$\hat{V}_2^* = \hat{V}_2^0(0) \tag{9}$$

In these equations, $\bar{D}_0$ is an effectively constant preexponential factor, $\hat{V}_I^*$ is the specific hole free volume of component I required for a jump, ω_I is the mass fraction of component I, T_{gI} is the glass transition temperature of pure component I, T is the temperature, and E^* is an energy parameter defined elsewhere.[1] Also, $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, $\hat{V}_{FH2}$ is the specific hole free volume of the equilibrium liquid polymer at any temperature, f_{H2}^G is the fractional hole free volume of the polymer at its glass transition temperature T_{g2}, γ represents an average overlap factor for the mixture, and γ_I represents the overlap factor for the free volume of pure component I. Furthermore, K_{11} and K_{21} are free-volume parameters for the solvent, K_{12} and K_{22} are free-volume parameters for the polymer, $\hat{V}_I^0(0)$ is the specific volume of component I at 0 K, $\hat{V}_2^0(T_{g2})$ is the specific volume of the liquid polymer at T_{g2}, α_{C2} is the thermal expansion coefficient for the polymer for the sum of the specific occupied volume and the specific interstitial free volume, and ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. Finally, α_2 is the thermal expansion coefficient for the equilibrium liquid polymer. In eqs 3 and 7, an average value of α_2 above T_{g2} is used. In eq 4, a temperature-dependent $\alpha_2(T)$ should be used if the appropriate data are available.

From the above equations, it is evident that the dependence of D_1 on ω_1 and T for rubbery polymer−solvent systems can be computed if the following parameters are available: $\bar{D}_0$, E^*, $\hat{V}_1^0(0)$, $\hat{V}_2^0(0)$, ξ, K_{11}/γ_1, $K_{21} - T_{g1}$, K_{12}/γ_2, K_{22}, T_{g2}, $\hat{V}_2^0(T_{g2})$, and $\alpha_2(T)$. Furthermore, it has been shown elsewhere[2] that these parameters are sufficient for the calculation of D_1 for glassy polymer−solvent systems. All of the above parameters, with the exception of ξ and E^*, can be determined using generally available data for the pure components. A parameter evaluation scheme has been presented elsewhere,[1] and it is noted there that as few as two diffusivity data points can be used to determine ξ and E^*. In the procedure proposed previously, ξ and E^* can be determined using measured solvent self-diffusion coefficients at $\omega_1 = 0$ and at two or more temperatures. Such a procedure can be easily applied to a inverse gas chromatography experiment where infinite dilution diffusion coefficients can be measured over relatively wide temperature ranges. In addition, it is possible to obtain $D_1(\omega_1{=}0)$ values for determining ξ and E^* by extrapolating diffusivity data collected using a high-temperature vapor sorption experiment. However, it is usually difficult to extract $D_1(\omega_1{=}0)$ values from a low-temperature vapor sorption experiment because the strong concentration dependence of diffusion coefficients near $\omega_1 = 0$ effectively precludes any definitive extrapolation to $\omega_1 = 0$. Furthermore, solvent self-diffusion data, measured using NMR experiments for moderate to high solvent concentrations (typically for $\omega_1 > 0.1$), cannot be used because extrapolation to $\omega_1 = 0$ is again not feasible.

The purpose of this note is to present an alternative method for determining ξ and E^* from solvent self-diffusion data. This procedure, which utilizes at least two $D_1 - \omega_1$ data points at a *single* temperature, can be used to analyze NMR self-diffusion experiments and both low- and high-temperature vapor sorption experiments. The proposed procedure thus permits the utilization of a wider variety of data sets in the evaluation of ξ and E^*. This procedure is presented and illustrated in the next section.

Table 1. Evaluation of Parameters

system	temp (°C)	expt	evaluation method	ξ	E^* [kcal/(g mol)]
polystyrene−toluene	160, 170, 178	vapor sorption	temp dependence of D_1 ($\omega_1 = 0$)	0.575	0
polystyrene−toluene	115	NMR	concn dependence at single T	0.540	0.08
polystyrene−ethylbenzene	130, 140	vapor sorption	temp dependence of D_1 ($\omega_1 = 0$)	0.590	0.61
polystyrene−ethylbenzene	100	NMR	concn dependence at single T	0.583	0.42

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Evaluation of Parameters

The concentration dependence of D_1 at a single temperature can be measured either by using an NMR experiment to directly measure the solvent self-diffusion coefficient D_1 or a vapor sorption experiment to measure the concentration dependence of the mutual diffusion coefficient D. In the latter case, it is possible to then convert[3] D to D_1; it is preferable to do this conversion at relatively low values of ω_1. The D_1 versus ω_1 data at a single temperature can then be used to determine ξ and E^* by writing eq 1 in the following form for temperatures above T_{g2}:

$$Y = \xi X + \frac{E^*}{RT} \tag{10}$$

$$Y = -\ln D_1 + \ln \bar{D}_0 - \frac{\omega_1 \hat{V}_1^*}{\hat{V}_{FH}/\gamma} \tag{11}$$

$$X = \frac{\omega_2 \hat{V}_2^*}{\hat{V}_{FH}/\gamma} \tag{12}$$

Both Y and X can be calculated using D_1 versus ω_1 data, eqs 2, 3, and 6–9, and the following previously determined parameters: $\hat{V}_1^0(0)$, $\hat{V}_2^0(0)$, $\bar{D}_0$, K_{11}/γ_1, $K_{21} - T_{g1}$, K_{22}, K_{12}/γ_2, $\hat{V}_2^0(T_{g2})$, T_{g2}, and α_2. Self-diffusion data above T_{g2} are used to avoid having to estimate $\alpha_2(T)$ below T_{g2}. Clearly, these data can be put in a straight-line form with a slope equal to ξ and an intercept equal to E^*/RT.

The proposed method is illustrated using self-diffusion data for the polystyrene–toluene and polystyrene–ethylbenzene systems. The free-volume parameters ξ and E^* were previously determined[1] for these systems by using $D_1(\omega_1{=}0)$ data obtained over a small temperature range from a vapor sorption experiment and by using the previous parameter evaluation procedure. The results are summarized in Table 1. The ξ and E^* parameters for these two systems can also be determined by using the new method and D_1 versus ω_1 data at a single temperature. For the polystyrene–toluene system, three D_1 data points[4,5] at 115 °C were used with eq 10, and for the polystyrene–ethylbenzene system, two D_1 data points[6] at 100 °C were used in the parameter evaluation. The new procedure based on eq 10 was used to evaluate ξ and E^* values for each system, and these results are presented in Table 1.

There is reasonably good agreement between the parameters evaluated using the previous temperature-dependence method and the present concentration-dependence method, even though both the methods and data sets used are very different. This agreement not only provides some verification of the general applicability of the free-volume theory of diffusion, but it suggests that the proposed method based on the concentration dependence of D_1 is a viable alternative to the previous method based on the temperature dependence of D_1. Furthermore, the present method can be used to extract ξ and E^* from NMR data and from both low- and high-temperature vapor sorption data, and data are needed only at one temperature. In addition, no extrapolation of data is required. Consequently, it is fair to conclude that the proposed method is an attractive alternative which provides increased flexibility in the parameter evaluation scheme.

Finally, we note that Waggoner et al.[7] have suggested a method of determining ξ *only* based on using the concentration dependence of D_1 and on using the value of D_1 for the pure solvent as a reference. This method assumes that the polymer contribution to the free volume is negligible.

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References and Notes

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