Effect of Solvent Size on Diffusion in Polymer–Solvent Systems

INTRODUCTION

In a new version of the free-volume theory of diffusion,[1–5] the following expression has been derived for D_1, the self-diffusion coefficient of the solvent:

$$D_1 = D_{01} \exp[-\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)/\hat{V}_{FH}] \tag{1}$$

where $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, $\hat{V}_I^*$ is the specific critical hole free volume of component I required for a jump, ω_I is the mass fraction of component I, γ is an overlap factor which is introduced because the same free volume is available to more than one molecule, and D_{01} is a preexponential factor which is assumed to be independent of temperature. Also, ξ is given by

$$\xi = \hat{V}_1^* M_{j1} / \hat{V}_2^* M_{j2} \tag{2}$$

where M_{j1} is the molecular weight of a solvent jumping unit and M_{j2} is the molecular weight of a polymeric jumping unit. The parameter ξ is clearly the ratio of the critical molar volume of a solvent jumping unit to the critical molar volume of the jumping unit of the polymer. Consequently, it is primarily through this quantity that solvent size influences the diffusion process.

The parameter ξ can conveniently be determined by considering the temperature dependence of the mutual diffusion coefficient D in the limit of zero mass fraction of solvent. At this limit, we can write eq. (1) in the usual form[4]

$$\ln D = \ln D_1 = \ln D_{01} - \gamma \hat{V}_2^* \xi / K_{12}(K_{22} + T - T_{g2}) \tag{3}$$

where T_{g2} is the glass transition temperature of the pure polymer, and K_{22} and $\gamma \hat{V}_2^*/K_{12}$ are simply related[2] to the Williams–Landel–Ferry (WLF) contants C_1^g and C_2^g of the polymer

$$K_{22} = C_2^g \tag{4}$$

$$\gamma \hat{V}_2^*/K_{12} = 2.303 \, C_1^g C_2^g \tag{5}$$

The definitions of K_{12} and K_{22} in terms of the volumetric properties of the polymer are given elsewhere,[4] and values of C_1^g and C_2^g have been tabulated[6] for a large number of polymers. Consequently, if diffusivity data are available for a polymer–solvent system in the limit of zero solvent mass fraction, it is evident from eq. (3) that a plot of $\ln D$ vs. $1/(K_{22} + T - T_{g2})$ yields values of D_{01} and $\gamma \hat{V}_2^* \xi / K_{12}$ if free volume theory satisfactorily describes the diffusion process. The parameter ξ can then be determined using eq. (5).

The apparent or effective activation energy E_D for diffusion in the limit of zero solvent concentration is defined by

$$E_D = RT^2 \left(\frac{\partial \ln D}{\partial T} \right)_P \tag{6}$$

and it is related to free volume parameters by the following expression:

$$E_D = \frac{RT^2(\gamma \hat{V}_2^* \xi / K_{12})}{(K_{22} + T - T_{g2})^2} \tag{7}$$

Hence, the effect of solvent size on the diffusion process can be conveniently examined by comparing effective activation energies at a particular temperature for various solvents diffusing in the same polymer, and this is the procedure usually followed in the diffusion literature.

There appear to be two conflicting theories concerning the variation of E_D with solvent size, the ceiling value hypothesis and a hypothesis based on free volume theory. A number of investigators[7–9] have proposed that as the molecular size of the penetrant increases, the activation energy will approach a limiting value which is associated with the self-diffusion process in the polymer. It is postulated that the activation energy for penetrants larger than a polymeric jumping unit will assume
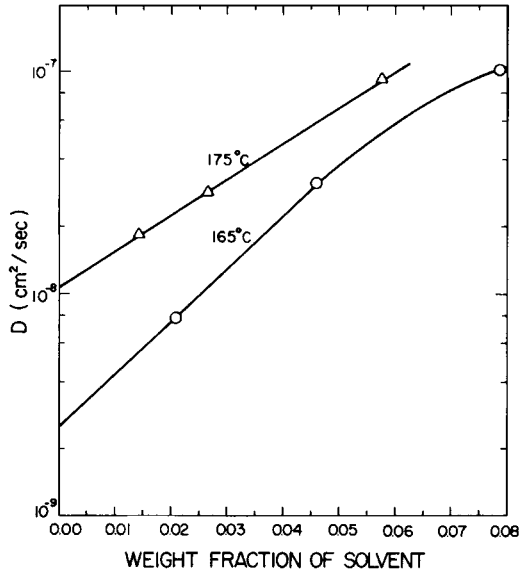
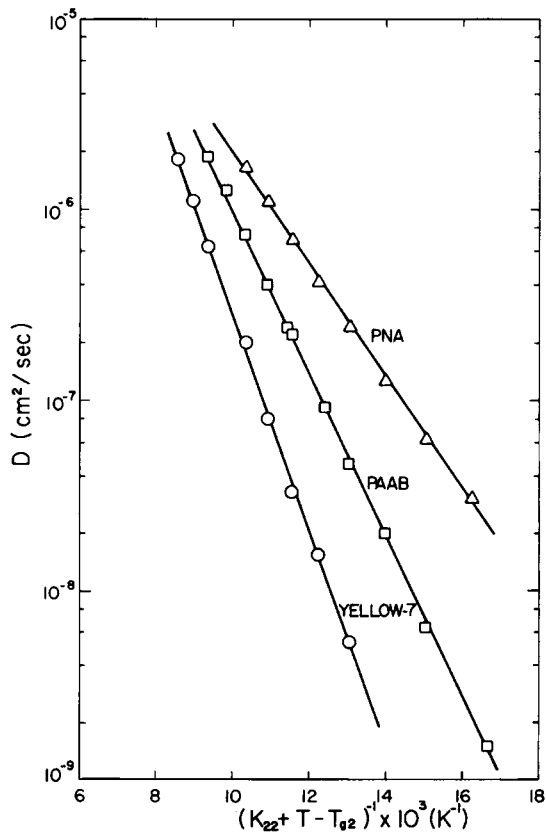Fig. 1. Diffusivity data for the triisopropylbenzene–polystyrene system.

Fig. 2. Free volume representation of PNA, PAAB, and Yellow 7 diffusion data in polystyrene.

TABLE I
Free Volume Parameters for Polystyrene–Solvent Systems

Solvent	$\gamma\hat{V}_2^*\xi/K_{12}$ (K)	ξ	Molar volume of solvent at 0 K (cm^3/g mole)
1. Hydrogen[a]	205	0.140	13.2
2. Methane[a]	161	0.111	27.2
3. Nitrogen[a]	252	0.172	21.1
4a. Methanol[a]	389	0.266	30.8
4b. Methanol[c]	337	0.231	30.8
5. Ethylene[a]	266	0.182	36.5
6. Carbon dioxide[a]	409	0.280	33.9
7. Ethanol[a]	467	0.320	48.1
8. Methylene chloride[a]	534	0.365	49.7
9. Ethyl bromide[a]	578	0.396	55.4
10. Pyridene[a]	734	0.503	67.2
11. Chloroform[a]	711	0.487	60.9
12. n-Propyl chloride[a]	760	0.521	66.6
13. Benzene[a]	778	0.533	70.4
14. Fluorobenzene[a]	800	0.548	75.0
15. n-Pentane[a]	617	0.422	83.6
16. Toluene[a]	996	0.682	84.4
17. Ethylbenzene[a]	1070	0.729	98.5
18. PNA[b]	687	0.470	96.6
19. PAAB[b]	991	0.678	155
20. Yellow 7[b]	1340	0.920	228
21. Triisopropylbenzene[c]	1900	1.300	197

[a] Source of data is ref. 4.
[b] Solvents studied by Masuko et al. (ref. 11).
[c] Solvents studied in the present investigation.

a ceiling value, independent of solvent size, since the movement of such penetrants is controlled by the motions of polymer molecules. On the other hand, in a strict interpretation of free volume theory, it is assumed that no energy is required for the redistribution of free volume since it is expected that higher-order energy terms are small.[10] Under this hypothesis, the energetics of polymer molecules do not influence E_D, and free volume theory predicts that ξ, and hence E_D, should increase indefinitely as the size of a solvent jumping unit increases. However, E_D or $\gamma\hat{V}_2^*\xi/K_{12}$ will not necessarily increase with an increase in the size of an entire solvent molecule since some solvents may move in a segmentwise manner,[5] with jumping units which constitute only a portion of the solvent molecule.

These two theories have been critically examined elsewhere[5] in light of the available experimental evidence, and it was concluded that the available diffusion data did not permit a definitive statement to be made on the behavior of ξ or E_D for solvent molecules with large jumping units. Leveling of the activation energy with the solvent molar volume has been reported for solvent diffusion in poly(methyl acrylate), but this can be attributed to segmentwise motion in a homologous series of solvents. In addition, the leveling of the activation energy observed for solvent diffusion in polyisobutylene can very probably be again attributed to the existence of segmentwise movement for large and sufficiently flexible solvents. It is evident that a decision could be made on whether the ceiling value hypothesis or the free volume interpretation were valid if data were available on the temperature dependence of D for a solvent which was not capable of segmentwise movement and which had a molar volume which was significantly larger than that of the polymeric jumping unit. Furthermore, the data should be taken at temperatures which are less than 100°C above the polymer glass transition temperature so that the temperature dependence of D is not complicated by energy effects.[5] The purpose of this note is to present polymer–solvent diffusion data for such a penetrant and thus permit a choice to be made between the ceiling value and free volume theories.
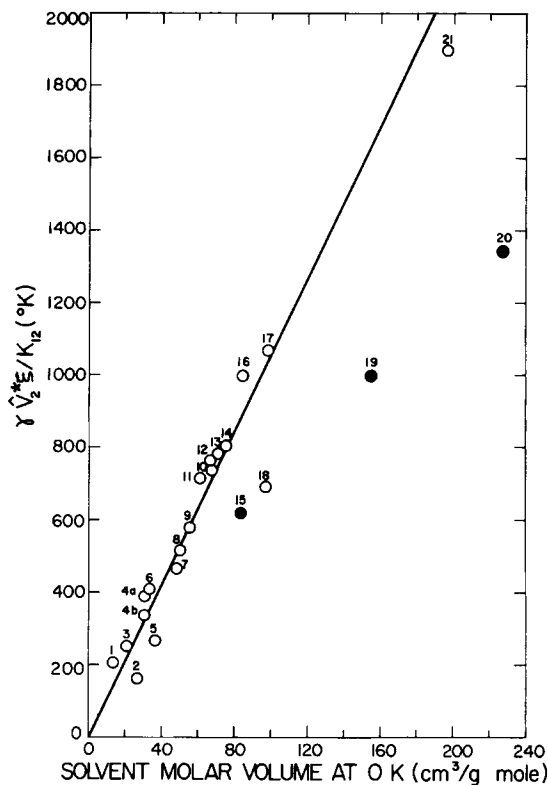
Fig. 3. Variation of $\gamma \hat{V}_2^* \xi / K_{12}$ with molar volume of the solvent at 0 K for polystyrene–solvent systems. Numbers of solvents correspond to those in Table I. Open circles represent solvents which might be expected to move as single units. The least-squares line was based on data from solvents 1–14, 16, 17, and 21.

RESULTS AND DISCUSSION

Since diffusivity data are available for 20 solvents in polystyrene,[4,11] it was decided to study the temperature dependence of the diffusion of an appropriate solvent in this polymer. From the previous diffusion data for polystyrene, it can be shown easily that the molar volume of the polystyrene jumping unit at 0 K can be estimated to be 139 cm^3/g mole. Hence, the solvent triisopropylbenzene is appropriate for testing the above theories since it has an estimated[12–14] molar volume at 0 K of 197 cm^3/g mole and a single ring structure and branched side chains which preclude significant segmentwise motion. Diffusivity data were collected as a function of concentration at 165 and 175°C for the triisopropylbenzene–polystyrene system using a quartz spring balance,[15–17] and the data are presented in Figure 1. The values of D_{01}, $\gamma \hat{V}_2^* \xi / K_{12}$, and ξ derived from the estimated values of the diffusivity at zero solvent mass fraction are presented in Table I.

Table I also includes the results for the 17 solvents considered earlier[4] and the recent data of Masuko et al.[11] for the diffusion of three dyes in polystyrene. The data of these investigators are used to form the type of plot suggested by eq. (3) for each of the three dyes, and these graphs are presented in Figure 2. It is evident from this figure that free volume theory provides an excellent representation of the temperature dependence of D for these three penetrants. It should also be noted from Table I that the molar volumes at 0 K for two of the three dyes are larger than that of the polystyrene jumping unit. However, it is reasonable to expect that PAAB and Yellow 7 move in a segmentwise manner so that the molar volumes at 0 K of the actual solvent jumping units for these materials may be lower than that for the polymer. Since these dye molecules probably have a rigid, rodlike structure, the segmentwise movement in this case refers to the possibility that only part of the rod is effectively displaced in a direction parallel to its axis.

It can be easily shown[4,5] that $\gamma \hat{V}_2^* \xi / K_{12}$ should be a linear function of the molar volume at 0 K of the jumping unit of the solvent. Hence, a plot of $\gamma \hat{V}_2^* \xi / K_{12}$ versus the molar volume at 0 K of the

entire solvent molecule should be a straight line through the origin for all solvents which jump as single units. If free volume theory is valid, the same straight line should represent all such solvents regardless of whether they are bigger or smaller than the polymeric jumping unit. Solvents which have jumping units smaller than the entire solvent molecule will of course have values of $\gamma \hat{V}_2^* \xi / K_{12}$ smaller than those predicted by this linear plot.

A plot of $\gamma \hat{V}_2^* \xi / K_{12}$ versus the solvent molar volume at 0 K is presented in Figure 3. A straight line through the origin provides a good representation of the diffusion behavior of 17 of the 21 solvents tested, including the large penetrant triisopropylbenzene. It is reasonable to expect that three of the four remaining solvents, n-pentane, PAAB, and Yellow 7, move in a segmentwise manner with jumping units smaller than the solvent molecule, and the deviations of the data for these solvents (the solid circles in Fig. 3) from the linear plot are expected. The only solvent that has an unexplained deviation from the straight line is PNA, and it could possibly also undergo significant segmentwise movement.

Only one of the 21 solvents considered has a jumping unit larger than that of the polymer, the solvent triisopropylbenzene. The fact that $\gamma \hat{V}_2^* \xi / K_{12}$ and, hence, E_D increase linearly with solvent molar volume, even for a solvent which is significantly larger than the polymeric jumping unit, is a clear indication that free volume theory correctly describes size effects in polymer–solvent diffusion. Hence, we conclude that the activation energy E_D for diffusion in polymer–solvent systems will increase indefinitely as the size of the solvent jumping unit increases rather than reach a ceiling value which characterizes the movement of polymeric jumping units.

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