Gas Chromatographic Measurements of Infinite Dilution Diffusion Coefficients of Volatile Liquids in Amorphous Polymers at Elevated Temperatures

DAVID S. HU, CHANG DAE HAN,* and LEONARD I. STIEL,
Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201

Synopsis

Measurements were made of infinite dilution diffusion coefficients of volatile liquids in amorphous polymers at elevated temperatures, using inverse gas chromatography. The liquids used were benzene, toluene, ethylbenzene, and n-decane. The polymers used were polystyrene and poly(vinyl acetate), and temperatures ranged from $30°C$ to $120°C$ above the glass transition temperatures of the polymers. Packed chromatographic columns were used to obtain data of the variation of the plate height with the average gas velocity, which was then used to determine diffusion coefficients with the aid of the van Deemter equation. In the present investigation, we have used different sizes of glass beads (0.3, 0.5, 0.6, and 1.0 mm in diameter), depending on the system temperature and the polymer/solute pair chosen. An attempt was made to correlate the diffusion coefficient D measured at various temperatures T, using $\ln D\zeta$ as ordinate and $1/[(K_{22} + T - T_{g2})/T_c]$ (hereafter referred to as the reciprocal of reduced free volume temperature, $1/T_{RF}$) as abscissa, in which $\zeta = M^{1/2}/T_c^{1/2}V_c^{1/3}$, M being the molecular weight, T_c the critical temperature, and V_c the critical volume of the solute, K_{22} is a free volume parameter of the polymer, and T_{g2} is the glass transition temperature of the polymer. It has been found that such plots give rise to two linear regions having different slopes, separated by a critical value of $1/T_{RF}$. The critical value of $1/T_{RF}$ is found to be insensitive to the type of solute and the type of polymer used. We have concluded that the infinite dilution diffusion coefficient of volatile liquids in amorphous polymers is controlled predominantly by the free volume of polymer above a critical value of $1/T_{RF}$, but energy effects are significant below the critical value of this parameter. In order to apply the generalized relationships in conjunction with gas chromatographic measurements, the results of this study indicate that, for values of $1/T_{RF}$ larger than a critical value, which is approximately 4.8, the following expression, $\ln D\zeta = \alpha + b/T_{RF}$, may be used to predict infinite dilution diffusion coefficients of volatile liquids in amorpous polymers at elevated temperatures, in which α is a constant, independent of the type of solute, and b is approximately a constant for a given polymer in the free volume region, independent of the type of solute. More experimental studies are needed, particularly for temperatures higher than those reported in this study, to corroborate and/or extend the correlations presented here.

INTRODUCTION

The diffusivity of gases and volatile solvents in molten polymers is an important transport property in the control of thermoplastic foam and polymer devolatilization processes. In the production of thermoplastic foams, either by means of foam extrusion or structural foam injection molding, a

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*To whom correspondence should be addressed.

blowing agent in the form of gas or volatile liquid is injected into a molten polymer under high pressure. As the pressure is decreased during the flow of the mixture in an extrusion die or in a runner of the mold, gas bubbles are nucleated which then grow by the diffusion of the blowing agent. As one may surmise, the rate of bubble growth (hence the cell size and its distribution in extruded or molded foam products) is greatly influenced by the diffusivity of the blowing agent in the molten polymer.[1]

The removal of residual solvent or monomer from polymerization reactor products is referred to as polymer devolatilization. The bulk polymerization product contains a small amount of unreacted monomer, which is to be removed to the level that would be acceptable for subsequent processing operations or specified by environmental and health hazards. Because of the relatively small amount of unreacted monomer remaining in the bulk polymerization product, it is generally considered that removal of monomer is primarily a diffusion-controlled process. It can be surmised then that information on the diffusion coefficient of monomer or solvent, hereafter termed volatiles, in the molten polymer is very essential for designing polymer devolatilizers and for predicting the performance of polymer devolatilization processes. The recent monograph by Biesenberger and Sebastian[2] has summarized very well the importance of various thermodynamic and transport properties relevant to polymer devolatilization processes.

Most of the available data on diffusion coefficients of volatile liquids or gases in molten polymer have been obtained by sorption experiments[3-11] which are time-consuming and require extensive data analysis. However, the sorption technique has the advantage in that it allows one to determine diffusion coefficients at finite concentrations of volatile liquids or gases. In recent years, gas chromatographic studies with packed or open columns, commonly referred to as inverse gas chromatography (IGC), have found wide utility for the measurement of diffusion coefficients of gases and volatile liquids in molten polymers.[12-20] This technique is promising since it enables the rapid determination of values of diffusion coefficients. However, it is applicable only to solutes at *infinite* dilution. At the same time, the diffusivity information obtained is useful for understanding the performance of devolatilizers or for controlling devolatilization operations.

Having realized that there is considerable uncertainty concerning the accuracy of the IGC technique and the method for the analysis of experimental data on diffusion coefficients, we have very recently developed procedures to more effectively utilize this approach. Experimental values of diffusion coefficients have been obtained for the solutes benzene, toluene, ethylbenzene, and *n*-decane in polystyrene and poly(vinyl acetate) over wide ranges of temperatures, from 30°C to 120°C above the glass transition temperatures of the polymers. In analyzing our experimental data, we have extended the Vrentas-Duda free volume theory.

PREVIOUS EXPERIMENTAL STUDIES AND THEORETICAL BACKGROUND

In the early studies on the measurement of diffusion coefficients of gases and volatile solvents in molten polymers, high-pressure sorption techniques

were employed. Newitt and Weale[3] determined solubilities and diffusivities for hydrogen, nitrogen, carbon dioxide, and ethylene in polystyrene for 130–190°C and 80–300 atmospheres. Lundberg et al.[4] obtained data at elevated temperatures and pressures for methane in polystyrene and polyisobutylene. Durrill and Griskey[5] determined solubility and diffusivity data for a number of gases in polyethylene, polypropylene, polyisobutylene, polystyrene, and poly(methyl methacrylate) at 180°C and 20 atmospheres.

Zhurkov and Ryskin[6] and Ryskin[7] utilized sorption experiments to determine diffusivities at elevated temperatures for water and organic and nonpolar solvents in a number of polymers including poly(methyl methacrylate), polystyrene, and poly(vinyl acetate).

Duda and Vrentas[8] utilized a quartz spring sorption apparatus to determine the solubility and diffusivity of n-pentane in polystyrene at atmospheric pressure and 140–170°C. Diffusion measurements by a similar procedure were also made by Duda et al.[9,10] for ethylbenzene and toluene in polystyrene for temperatures to 178°C and pressures to atmospheric. Maxima in the diffusion coefficients at a weight fraction of solvent of about 0.3–0.4 were observed for the ethylbenzene/polystyrene and toluene/polystyrene systems. Ju et al.[11] also determined diffusivities by sorption experiments for toluene, chloroform, and tetrahydrofuran in poly(vinyl acetate) for temperatures to 48°C, for toluene and methanol in poly(methyl methacrylate) for 120–160°C, and for carbon disulfide·in polystyrene for 115–140°C.

Inverse Gas Chromatography

We will review below very briefly the inverse gas chromatographic (IGC) procedure for determining diffusion coefficients of volatile liquids or gases in molten polymers. For packed chromatographic columns, diffusion coefficients are determined from an analysis of the variation of the plate height H with the average gas velocity u, by the use of the van Deemter equation:[21]

$$H = A + B/u + Cu \qquad (1)$$

where A, B, and C are constants and the plate height H is determined from the width of the eluted solvent peak. The constant C in Eq. (1) accounts for mass transfer in the stationary polymer phase and is related to the diffusion coefficient D as follows:

$$C = \frac{qkf_m^2}{(1 + k)^2 D} \qquad (2)$$

where q is a shape factor accounting for the nonuniformity of the liquid film in the packed column, f_m is the film thickness at its deepest point, and k is the mass distribution ratio of the solute between the gaseous and liquid phases. At high flow rates, the second term in Eq. (1), representing diffusion in the gas phase, is small, and the constant C can be determined from the slope of a plot of H versus u.

Gray and Guillet[12] utilized chromatographic procedures to determine diffusion coefficients for several solutes in low-density polyethylene for tempera-

tures to 170°C. Best results were obtained with glass beads as the support. A uniform polymer film was assumed, and values of D were calculated from Eq. (2) with $q = 8/\pi^2$. The polymer film thickness f_m was obtained as:

$$f_m = (1/3)W(\rho_B/\rho_P)\bar{r} \tag{3}$$

where W is the coverage ratio of polymer to packing, $\bar{r}$ is the average radius of the beads, and ρ_B and ρ_P are the densities of the beads and polymer, respectively. A similar approach was taken by Braun et al.,[13] who used $q = 8/\pi^2$ for several hydrocarbons and stabilizers in low-density polyethylene for temperatures to 169°C.

Senich[16, 17] determined the diffusion coefficients of several solutes in polyethylene by gas chromatographic procedures. Glass beads were utilized, and it was assumed that all of the polymer accumulated at the contact points of the beads. In place of Eq. (2), the following relationship was used to relate the slope C in the plots of H versus u to the diffusion coefficient D:

$$C = \left(\frac{4\bar{r}^2 k}{120(1 + k)^2 D}\right)\left(\frac{W\rho_B}{18.75\rho_P}\right)^{1/2} \tag{4}$$

A similar approach was used by Hawkes and co-workers[14, 15] for diffusion coefficients in silicones and other liquid polymers.

Hawkes[22] has recently performed a critical evaluation of the applicability of Eq. (1). He showed that the constant A in Eq. (1) can be taken as zero, and that the constant q in Eq. (2) can vary from 2/15 for spherical beads of polymer to 2/3 for a uniform film. He also indicated that the constant C should include a contribution for mass transfer in the mobile gas phase.

Edwards and Newman[18] presented a mathematical analysis of the effect of mass transfer in the stationary phase on retention volumes obtained by gas chromatography in open capillary columns. It was found that the results lead to the following relationship for the variation of the specific retention volume V_g with carrier gas flow rate Q:

$$\ln V_g = c_1 + d_1 Q/V_g \tag{5}$$

where c_1 is the limiting value of the specific retention volume, and the constant d_1 is related to the diffusion coefficient D in the polymer phase as:

$$d_1 = B_1/L\mu DT \tag{6}$$

in which B_1 is a numerical constant, L the column length, μ the distance from the column center to the coated polymer surface, divided by the thickness of the polymer film, and T is the temperature. Edwards and Newman utilized the retention volume data of Lichtenthaler et al.[23] obtained with capillary columns for cyclohexane and benzene in polyisobutylene at 75°C.

Pawlisch and Laurence[20] developed a modified mathematical model for the diffusion of solutes at infinite dilution in thin, uniform polymer films coated on glass capillary columns. Measurements were made for benzene, toluene,

and ethylbenzene in polystyrene for 110–140°C. The resulting values of the diffusion coefficient were in good agreement with extrapolated values from sorption experiments.[8,9]

Free Volume Theories

The free volume concept has been used to describe the viscosity and self-diffusion of low molecular weight liquids. Cohen and Turnbull[24] developed a free volume theory to describe the molecular transport of a liquid consisting of hard spheres, by assuming that the molecular transport occurs by the movement of molecules into voids formed by redistribution of the free volume. Fujita[25,26] is the first to advance a theory for describing solvent–polymer diffusion that included concentration and temperature dependencies, using the free volume concept. According to Fujita,[26] the diffusion coefficient D of a diluent molecule in a polymer may be represented by

$$D = A_d RT \exp(-B_d/f) \tag{7}$$

in which A_d is a free volume parameter that depends primarily on the size and shape of the diluent molecule and hence may be independent of temperature and diluent concentration, B_d is a free volume parameter that represents the minimum hole required for a given diluent molecule to permit a displacement, R is the universal gas constant, T is the temperature, and f is the average fractional free volume of the system.

Vrentas and Duda[27] have developed improved free volume theories for predicting the concentration dependence of diffusion coefficients of solutes in molten polymers. Specifically, they assigned the parameter A_d in Eq. (7) to be the pre-exponential value of the solvent self-diffusion coefficient, and the parameter B_d to be a linear function of the closed-packing volume (i.e., volume of solvent occupied at 0°K). In a further study,[28] they made the following assumptions: (1) all thermal expansion coefficients of free volumes may be approximated by average values in the temperature range under consideration; (2) the partial specific volumes of polymer and solvent are independent of concentration so that the influence of volume change on mixing on the free volume of the system is considered to be negligible; (3) the solvent chemical potential in the mixture is given by the Flory-Huggins equation. On this basis, they obtained the following expression for the diffusion coefficient D

$$D = D_{o1}(1 - \Phi_1)^2(1 - 2\chi\Phi_1)\exp\left[-\frac{(w_1\hat{V}_1^* + w_2\xi\hat{V}_2^*)}{V_{FH}/\gamma}\right] \tag{8}$$

where

$$\frac{V_{FH}}{\gamma} = \frac{K_{11}}{\gamma}w_1(K_{21} + T - T_{g1}) + \frac{K_{12}}{\gamma}w_2(K_{22} + T - T_{g2}) \tag{9}$$

$$\Phi_1 = \frac{w_1\hat{V}_1^o}{w_1\hat{V}_1^o + w_2\hat{V}_2^o} \tag{10}$$

$$D_{o1} = D_o\exp(-E/RT) \tag{11}$$

in which Φ_1 is the volume fraction of solvent, χ is the interaction parameter for a given polymer-solvent system, w_i is the mass fraction of component i, $\hat{V}_i^*$ is the specific critical hole volume of component i required for a jump, ξ is the ratio of critical molar volume of solvent jumping unit to critical molar volume of jumping unit of polymer, V_{FH} is the average hole free volume per gram of mixture, γ is an overlap factor for free volume, K_{11} and K_{21} are free volume parameters of solvent, K_{12} and K_{22} are free volume parameters of polymer, T_{gi} is the glass transition temperature of component i, $\hat{V}_i^o$ is the partial specific volume of component i, D_o is a pre-exponential factor, E is the critical energy per mole needed to overcome attraction forces, and R is the universal gas constant. Vrentas and Duda[29] have presented procedures for evaluating and predicting the variation of diffusion coefficient D with temperature T and mass fraction w_i for a particular polymer-solvent system using Eq. (8).

At infinitely dilute concentration (i.e., for $\Phi_1 = w_1 = 0$) of volatile component, Eq. (8) reduces to:

$$\ln D = \ln D_o - \frac{E}{RT} - \frac{\gamma \hat{V}_2^* \xi / K_{12}}{K_{22} + T - T_{g2}} \tag{12}$$

When the magnitude of the term E/RT in Eq. (12) is negligibly small compared to other terms (i.e., $E \approx 0$), Eq. (12) reduces to

$$\ln D = \ln D_o - \frac{\gamma \hat{V}_2^* \xi / K_{12}}{K_{22} + T - T_{g2}} \tag{13}$$

in which K_{22} and T_{g2} (the glass transition temperature) characterize properties of the polymer, and D_o and $\gamma \hat{V}_2^* \xi / K_{12}$ are properties of the polymer-solvent system. Note that the parameters K_{22} and $\gamma \hat{V}_2^* \xi / K_{12}$ are simply related to the WLF constants of the polymer.[30]

Ju et al.[11] showed that, for a particular polymer-solute system, $\gamma \hat{V}_2^* \xi / K_{12}$ in Eq. (13), which has the dimension of temperature, can be estimated from a linear relationship between values of this constant for the polymer and the molar volume of the solute at $0°K$, as estimated by group contribution methods.

EXPERIMENTAL

Materials

In this study, experimental values of diffusion coefficients have been obtained for a number of solutes in polystyrene (PS) (Dow Chemical, STYRON 685D) and poly(vinyl acetate) (PVAc) (Polysciences). The glass transition temperatures of these polymers, determined in this study using differential scanning calorimetry (DSC), are $100.8°C$ for PS, and $32.8°C$ for PVAc at a heating rate of $2°C/min$. The solutes used were benzene, toluene, ethylbenzene, and and n-decane. All solvents used were reagent grade.
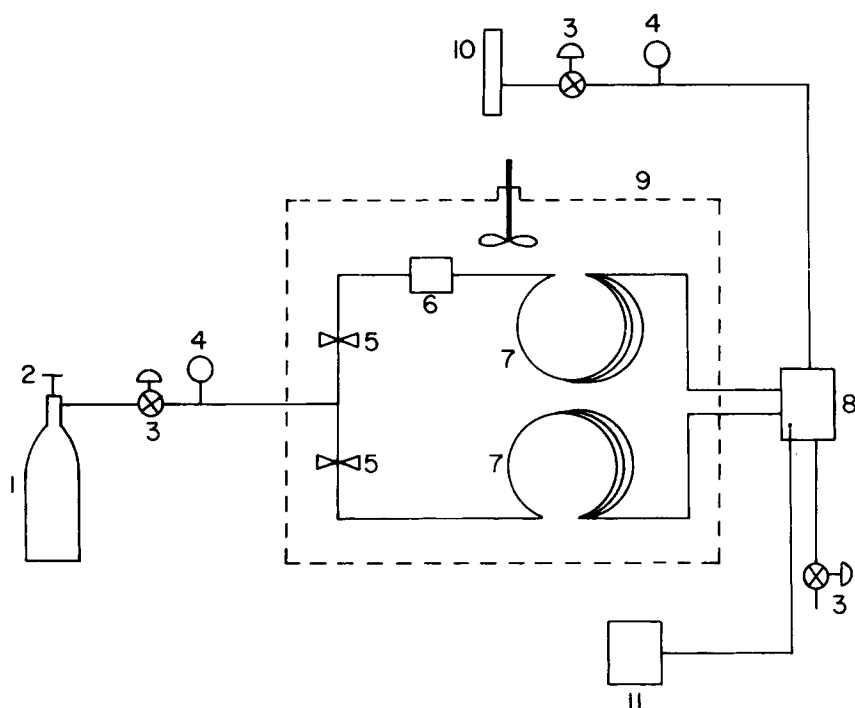
Fig. 1. Schematic of gas chromatograph system: (1) helium tank; (2) pressure regulator; (3) needle valve; (4) pressure gauge; (5) metering valve; (6) injection port; (7) coiled column; (8) detector; (9) column oven; (10) bubble flow meter; (11) recorder or integrator.

Procedures

A schematic diagram of the experimental apparatus is shown in Figure 1. A weighed quantity of the polymer is totally dissolved in a suitable solvent such as chloroform or benzene. Glass beads with average diameters of 0.3–1.0 mm were utilized to provide a suitable range of support particles. A summary of the column sizes, glass bead sizes, and temperatures employed in the experiments is presented in Table I. The glass beads are mixed with the polymer solution and dried in a vacuum oven for 24 h. The coated support is then packed into copper tubing 1.52 m long and 6.35 mm in diameter. The coverage ratio is approximately 0.5%. The column is then placed into a dual-column GOWMAC 69-560 gas chromatograph with a thermal conductivity detector. The output of the detector is monitored with a Hewlett-Packard reporting integrator, Model 3390A. The helium carrier gas is controlled with two metering valves at the column inlets and needle valves at the column outlets. The gas flow rate is measured with a 10 cc soap-bubble flowmeter. The pressures of the gas at the inlet and outlet of the chromatograph are measured with gauges accurate to 0.25 psia. For the present experiments the inlet pressures are approximately 30 psia with maximum column pressure drops of 2 psia. The oven temperature is controlled with a thermocouple and measured with an accurate thermometer.

For liquid solutes, a small amount of fluid (0.05 μL) is injected using a microsyringe with a repeating dispenser, while 10 μL of air (reference gas) are

TABLE I
Experimental Conditions Employed for Determining Diffusion Coefficients

Solute	Temperature (°C)	Glass bead diameter (mm)
Polystyrene		
Toluene	150–200	0.5, 0.6, 1.0
Ethylbenzene	150–200	0.6, 1.0
n-Decane	150–200	0.6, 1.0
Benzene	121–181	0.3, 0.5, 0.6, 1.0
Poly(vinyl Acetate)		
Toluene	105–150	0.5, 0.6, 1.0
Ethylbenzene	109–132	0.5, 0.6
n-Decane	90–160	0.3, 0.6, 1.0
Benzene	89–150	0.3, 0.5, 1.0

injected with a Hamilton syringe. Comparable results were obtained by the injection of the solutes as gases by the use of an eight-port gas sampling valve. The retention times t_g and t_r for the eluted solute and air as the reference gas from injection until peak detector responses are determined with the reporting integrator. The plate height H is determined from the integrator output as

$$H = (L/5.54)(W_{1/2}/t_g)^2 \tag{14}$$

where L is the length of the column and $W_{1/2}$ is the measured peak width at half the maximum height.

The velocity u at each flow rate is obtained from the column length and air retention time as

$$u = L/t_r \tag{15}$$

The diffusion coefficient D is calculated from Eq. (2) with k obtained from the following ratio extrapolated to zero flow rate:

$$k = (t_g - t_r)/t_r \tag{16}$$

The polymer film thickness is determined from Eq. (3).

RESULTS

Determination of Geometric Factor of the Stationary Phase in Van Deemter Equation

The elution data, including solute retention time, solute plate height, partition ratio of solute, and air retention time at various temperatures were obtained as functions of volumetric flow rate or linear carrier gas velocity. In all cases, the retention time of air was found to be a linear function of the reciprocal of volumetric flow rate. But the retention time of solute deviated slightly from linearity with an exponent for volumetric flow rate ranging from -1.04 to -1.08.

Diffusivity measurement by IGC has the uncertainty of the determination of the geometric factor q in Eq. (2). This is because the mean thickness of the polymer film (f_m) for Eq. (2) is difficult to determine accurately without knowing the geometry *a priori*, and is, for convenience, taken as that for the infinite plate. This is a valid assumption for very thin polymer films. Note that the value of q is also dependent upon the geometry, with a numerical value equal to 2/3 for a planar film, 1/12 for contact point geometry, and $8/\pi^2$ for a sphere,[22] that is, q is an empirical geometrical factor. Therefore, IGC cannot provide absolute values of diffusion coefficients unless one determines the numerical values of q by comparing the values of diffusion coefficients obtained by IGC with those determined by other independent methods, such as the sorption method.

In the present investigation, with polystyrene as the polymer substrate, experimental measurements were initially obtained for ethylbenzene and toluene at 150–175°C, using 0.3 mm diameter glass beads as the support. The resulting diffusion coefficients were compared with available data for these systems, obtained by extrapolation of the results of sorption experiments[31, 32] to infinite dilution of the solutes. It was found that, with this packing, the constant C in Eq. (1) is small, and diffusion in the polymer phase at some conditions was controlling only at the highest attainable velocities (approximately 15 cm/s). Subsequent measurements were made with 0.5, 0.6, and 1.0 mm diameter glass beads. More reproducible results were obtained with these columns, and reasonable agreement with the literature values resulted when the factor q in Eq. (2) was made equal to 1/6. A summary of the actual values of q obtained is presented in Table II. Additional measurements of diffusion coefficients in polystyrene were made with $q = 1/6$ and appropriate columns for benzene and n-decane.

TABLE II
Values of the Geometric Factor q Used for Determining the Diffusion Coefficient

Temp. (°C)	$\bar{r}$ (cm)	D (cm^2/s)	$f_m \times 10^4$ (cm)	q (dimensionless)
PS/Toluene				
175	0.03	2.6×10^{-7} [a]	5.368	0.159
175	0.05	2.6×10^{-7} [a]	8.915	0.146
160	0.025	9.2×10^{-8} [a]	4.504	0.172
PS/Ethylbenzene				
165	0.03	2.0×10^{-7} [a]	5.368	0.169
PVAc/Toluene				
110	0.025	3.0×10^{-8} [b]	4.151	0.103
PVAc/Benzene				
89	0.015	4.48×10^{-9} [c]	2.471	0.157
				Average 0.152

[a] Ref. 31.
[b] Ref. 32.
[c] Ref. 7.

TABLE III
Summary of the Diffusion Coefficients Determined in This Study

T (°C)	$\dfrac{1}{T_R}$	$\dfrac{10^3}{(K_{22} + T - T_{g2})}$	$\dfrac{1}{T_{RF}}$	$\log D$	$\ln D\zeta$
PS/Benzene					
129	1.397	13.038	7.328	−7.916	−21.066
135	1.377	12.092	6.797	−7.625	−20.395
150	1.328	10.235	5.763	−7.214	−19.452
160	1.297	9.285	5.219	−7.015	−18.992
170	1.268	8.496	4.776	−6.814	−18.529
181	1.237	7.770	4.368	−6.638	−18.125
PS/Toluene					
150	1.398	10.235	6.056	−7.304	−19.667
160	1.366	9.285	5.494	−7.049	−19.080
165	1.350	8.873	5.250	−6.655	−18.173
175	1.320	8.150	4.822	−6.560	−17.955
181	1.303	7.770	4.597	−6.569	−17.975
185	1.291	7.536	4.459	−6.614	−18.079
190	1.277	7.262	4.297	−6.500	−17.815
200	1.250	6.770	4.006	−6.478	−17.765
PS/Ethylbenzene					
150	1.458	10.235	6.316	−7.158	−19.338
165	1.408	8.873	5.475	−6.701	−18.284
175	1.377	8.150	5.029	−6.530	−17.891
180	1.362	7.831	4.832	−6.701	−18.285
190	1.332	7.262	4.481	−6.514	−17.855
200	1.304	6.770	4.178	−6.464	−17.738
PS/n-Decane					
150	1.459	10.235	6.321	−7.431	−19.977
160	1.426	9.285	5.734	−7.134	−19.293
165	1.409	8.873	5.480	−7.008	−19.005
175	1.378	8.150	5.033	−6.796	−18.516
182	1.357	7.710	4.762	−6.804	−18.546
186	1.344	7.479	4.619	−6.743	−18.407
190	1.333	7.262	4.485	−6.682	−18.265
200	1.305	6.771	4.181	−6.682	18.093
PVAc/Benzene					
89	1.552	9.416	5.293	−8.259	−21.857
95	1.527	8.913	5.010	−7.738	−20.656
100	1.506	8.532	4.796	−7.517	−20.147
110	1.467	7.861	4.419	−7.256	−19.546
115	1.448	7.564	4.252	−7.245	−19.522
120	1.429	7.288	4.097	−7.008	−18.977
130	1.394	6.803	3.823	−6.959	−18.863
140	1.360	6.369	3.580	−6.915	−18.761
150	1.328	5.981	3.362	−6.625	−18.094
PVAc/Toluene					
105	1.564	8.183	4.842	−7.517	−20.157
110	1.544	7.862	4.652	−7.316	−19.694
120	1.505	7.288	4.313	−7.042	−19.064
130	1.467	6.793	4.019	−6.832	−18.581
140	1.432	6.361	3.764	−6.686	−18.244
150	1.398	5.981	3.539	−6.623	−18.098

TABLE III
(Continued from previous page.)

T (°C)	$\dfrac{1}{T_R}$	$\dfrac{10^3}{(K_{22} + T - T_{g2})}$	$\dfrac{1}{T_{RF}}$	$\log D$	$\ln D\zeta$
PVAc/Ethylbenzene					
109	1.615	7.924	4.889	−7.445	−19.997
120	1.569	7.289	4.498	−7.178	−19.383
132	1.523	6.702	4.136	−6.825	−18.570
PVAc/n-Decane					
90	1.700	9.328	5.761	−8.189	−21.734
95	1.677	8.912	5.504	−8.149	−21.644
110	1.612	7.861	4.855	−7.299	−19.686
120	1.570	7.289	4.501	−7.082	−19.186
131	1.528	6.737	4.167	−6.793	−18.523
160	1.425	5.643	3.485	−6.754	−18.431
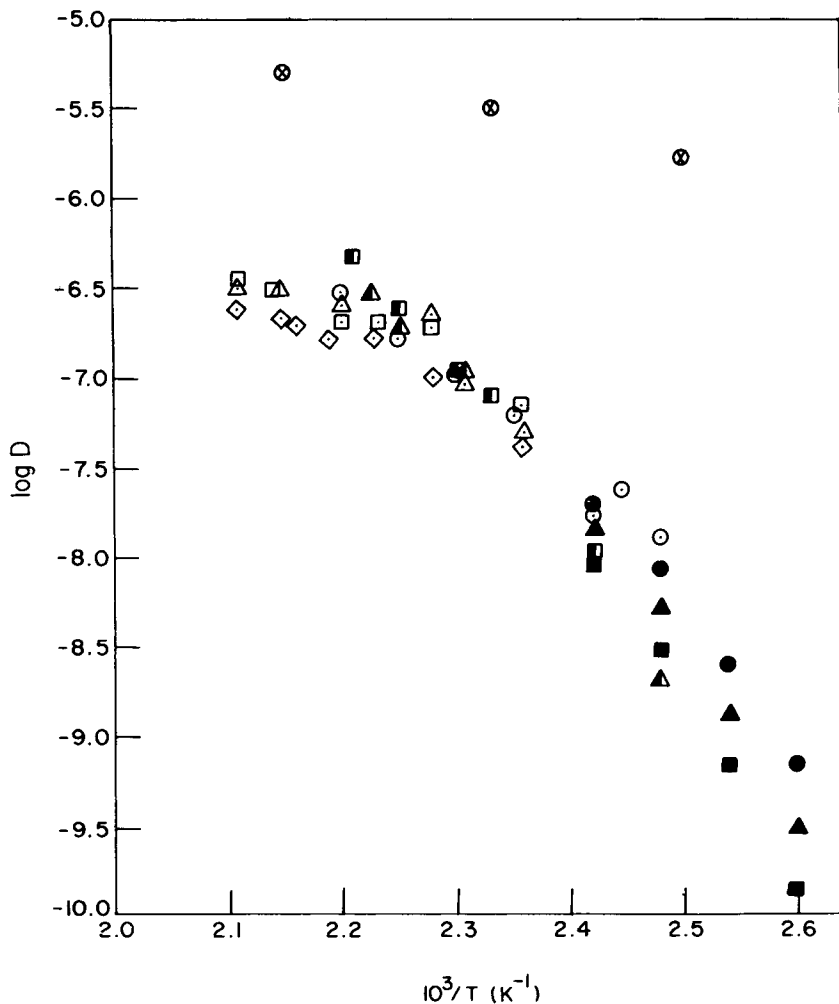
Fig. 2. Log D versus $1/T$ for various solutes in PS: (⊙) benzene; (△) toluene; (▢) ethylbenzene; (◇) n-decane; (●) benzene (Ref. 20); (▲) toluene (Ref. 20); (▲) toluene (Ref. 31); (■) ethylbenzene (Ref. 20); (▣) ethylbenzene (Ref. 31); (⊗) methane (Ref. 4).

Similarly, we determined the values of q for PVAc as polymer substrate, and benzene and toluene as solutes, by comparing our measurements with the literature data.[7,32] An average value of $q \approx 1/6$ was also obtained for the PVAc systems. It should be mentioned that errors of as much as 30% (for example, for the toluene/PVAc system in the temperature range 35–110°C) were introduced when the literature data were extrapolated to obtain values of the diffusion coefficient at infinite dilution. This is due to the fact that the concentration dependence of the diffusion coefficient deviates from linearity when the solute fraction is near zero. The values of q obtained are included in Table II. We have concluded that the use of $q \approx 1/6$ over the wide range of temperature investigated seems reasonable for the different polymer-solvent pairs employed. Additional measurements for PVAc systems were made for ethylbenzene and n-decane.
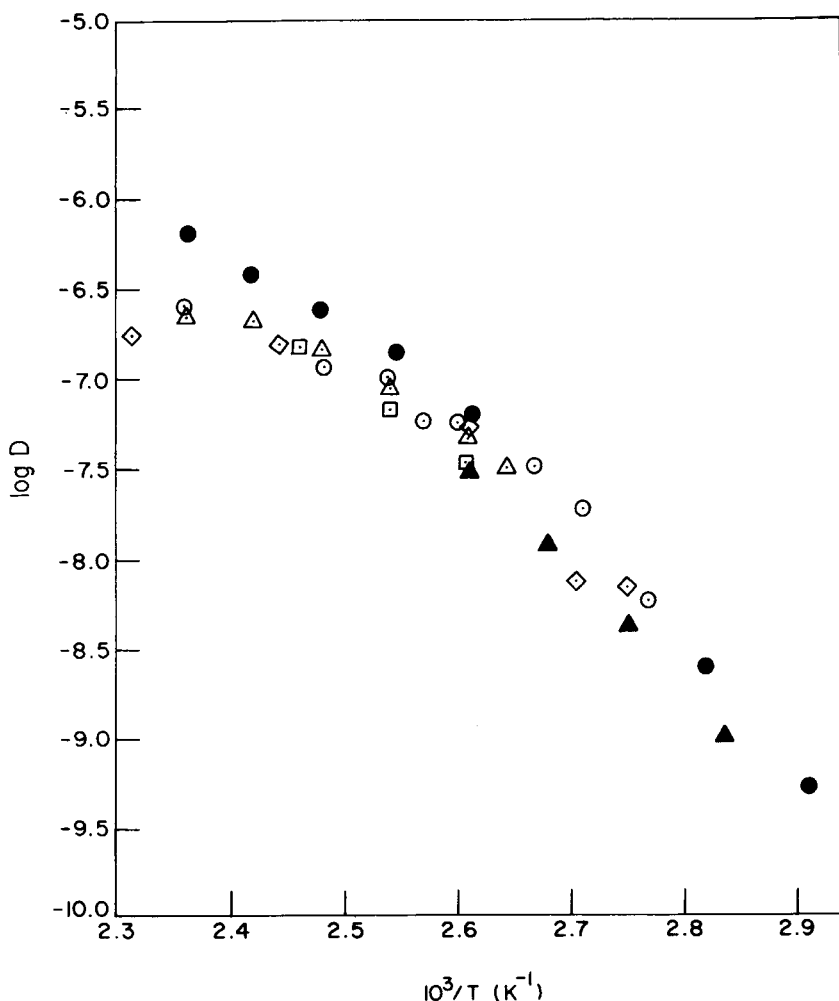
Fig. 3. Log D versus $1/T$ for various solutes in PVAc: (⊙) benzene; (△) toluene; (□) ethylbenzene; (◇) n-decane; (●) benzene (Ref. 7); (▲) toluene (Ref. 32).

At a constant coverage ratio of polymer to support, the measured diffusion coefficients were found to vary somewhat with the diameters of the glass beads utilized, and the values for 1.0 mm glass beads exhibited less of a temperature dependence. This behavior may be due to contributions of mass transfer in the gas phase to the constant C of Eq. (1), which increases with the diameter of the support particles. For molecules with low diffusion coefficients, such as n-decane, the slopes of the plots of H versus u [see Eq. (1)] are high for the columns having large diameter glass beads compared to those having small ones. The minimum values of H for this case occur at low velocities, and the slope C [i.e., the constant C of Eq. (1)] is lower at high velocities than at velocities in the vicinity of the minimum H. The slope determined at high velocities also does not pass through the origin as required by Eq. (1) with $A = 0$. This behavior indicates that there is an optimum chromatographic column for each solute-polymer system at each temperature level investigated. A sufficiently large value of the mass distribution ratio k is also required in order to permit the use of Eq. (2). Moreover, for polystyrene systems, this technique with packed chromatographic columns is limited to solutes of appreciable molecular size having $T_c > 500$ K.

Correlation with the Vrentas-Duda Free Volume Theory

The experimental values of diffusion coefficient obtained in this study are presented in Table III. Using this experimental data, and the data available in the literature, plots of $\log D$ versus $1/T$ are given in Figure 2 for PS and in Figure 3 for PVAc, with the four solutes employed. For comparison purposes, the literature data available for the same organic solutes and methane are given in these figures. It is seen in Figures 2 and 3 that the slope of the $\log D$ versus $1/T$ plots (i.e., the activation energy for diffusion) varies with temperature, indicating that an Arrhenius expression is not suitable for correlating infinite dilution diffusion coefficients of the four organic solutes and methane in PS and PVAc, in the range of temperature investigated, that is, $T_g < T < T_g + 120°C$. Note in Figure 2 that the methane data of Lundberg et al.[4] deviate considerably from the rest of the data points.

With the same data used in Figures 2 and 3, plots of $\log D$ versus $1/(K_{22} + T - T_{g2})$ were prepared with the aid of Eq. (13), and they are displayed in Figure 4 for PS, and in Figure 5 for PVAc. In preparing Figures 4 and 5, the values of K_{22} used are 47.7 K for PS and 46.0 K for PVAc, and the values of T_{g2} used are 100°C for PS and 33°C for PVAc. It should be mentioned that, using the data taken at temperatures below 178°C but above T_{g2} for PS, and at temperatures below $T_g + 80°C$ but above T_{g2} for PVAc, Duda and co-workers[9,10] have observed that such plots show a linear correlation, represented by Eq. (13). According to Eq. (13), the slopes in the $\log D$ versus $1/(K_{22} + T - T_{g2})$ plots are represented by $\gamma \hat{V}_2^* \xi / K_{12}$, in which γ represents the polymer-solvent interaction in the jumping process (describing the fact that the same free volume is available for more than one molecule), and $\hat{V}_2^* \xi / K_{12}$ represents an inherent polymer variable.

A comparison of Figure 4 with Figure 2, and Figure 5 with Figure 3, indicates that the introduction of free volume parameters of polymers leads to better correlations. However, the dependence of D on the structure of solute
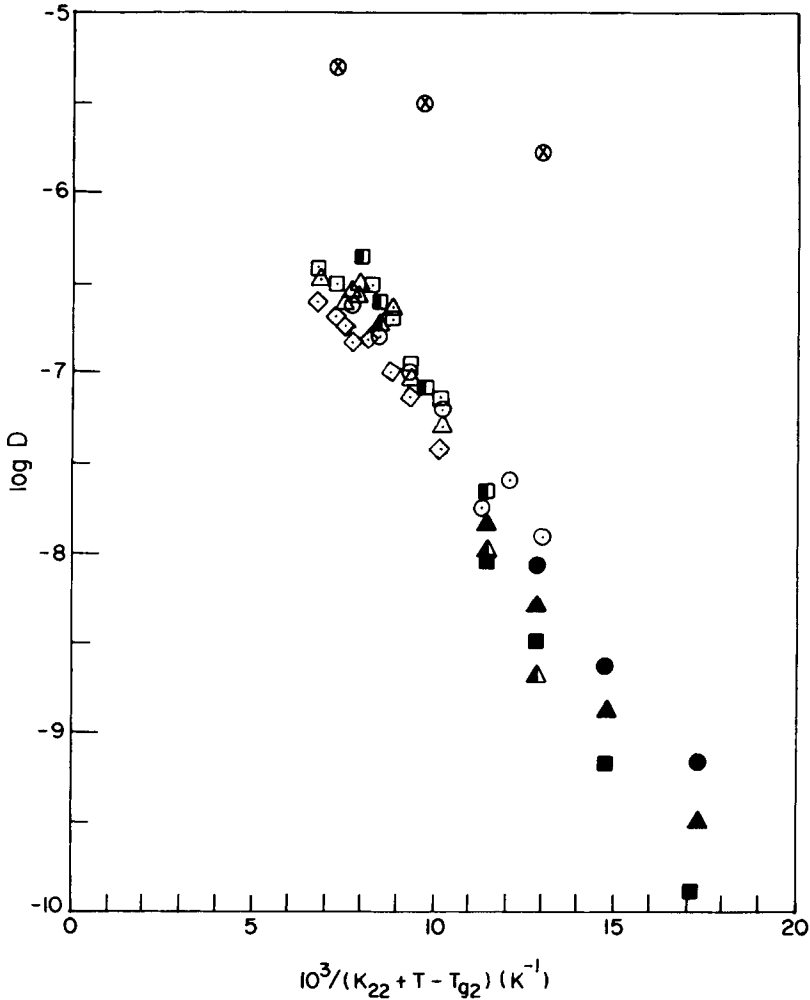
Fig. 4. Log D versus $1/(K_{22} + T - T_{g2})$ for various solutes in PS. Symbols are the same as in Fig. 2.

still remains strong for PS (see Fig. 4), while considerable improvement is seen for PVAc (see Fig. 5). Note in Figure 4 that the methane data of Lundberg et al.[4] still deviate considerably from the correlation suggested by Eq. (13).

In an attempt to correlate the structure of solvent to its self-diffusion coefficient in polymeric liquids, Kulkarni et al.[33] used the Lennard-Jones size parameter, together with Fujita's theory,[26] to investigate the effect of the molecular structure of the gas on the free volume parameters.

Correlation with a Generalized Vrentas-Duda Free Volume Relationship

In order to make the various quantities in Eq. (12) dimensionless, let us consider the following parameter ζ defined as

$$\zeta = M^{1/2}/\left(T_c^{1/2}\right)\left(V_c^{1/3}\right) \tag{17}$$
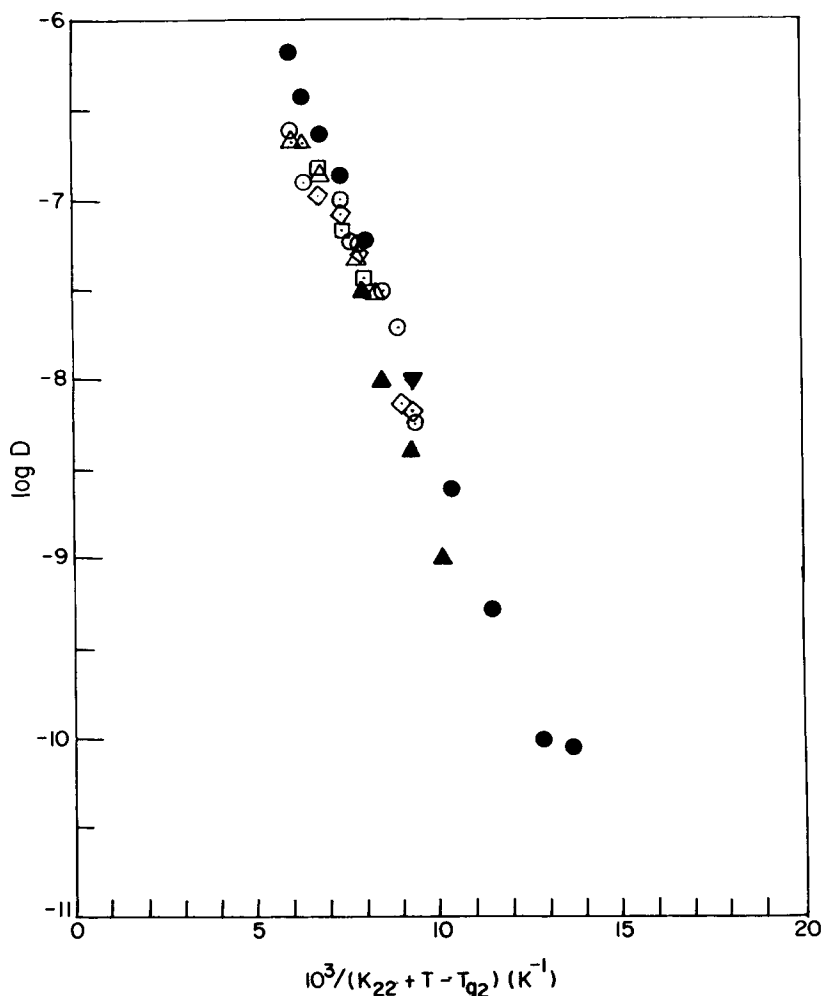
Fig. 5. Log D versus $1/(K_{22} + T - T_{g2})$ for various solutes in PVAc. Symbols are the same as in Fig. 3.

where M is the molecular weight of the solute, T_c is the critical temperature of the solute, and V_c is the critical volume of the solute. It can be shown that $D\zeta/R^{1/2}$ is a dimensionless quantity, R being the universal gas constant. It should be mentioned that earlier other investigators[34-36] also used the parameter ζ for correlating the self-diffusion coefficient of small molecules to their critical properties. Note that the group $D\zeta$ may be used as a *reduced* diffusion coefficient to correlate the solute self-diffusion coefficient in molten polymers.

The use of the parameter ζ defined by Eq. (17) and the critical temperature T_c of solute in Eq. (12) yields the following expression, hereafter referred to as a generalized Vrentas-Duda free volume relationship,

$$\ln D\zeta = a + b/T_{RF} + c/T_R \qquad (18)$$
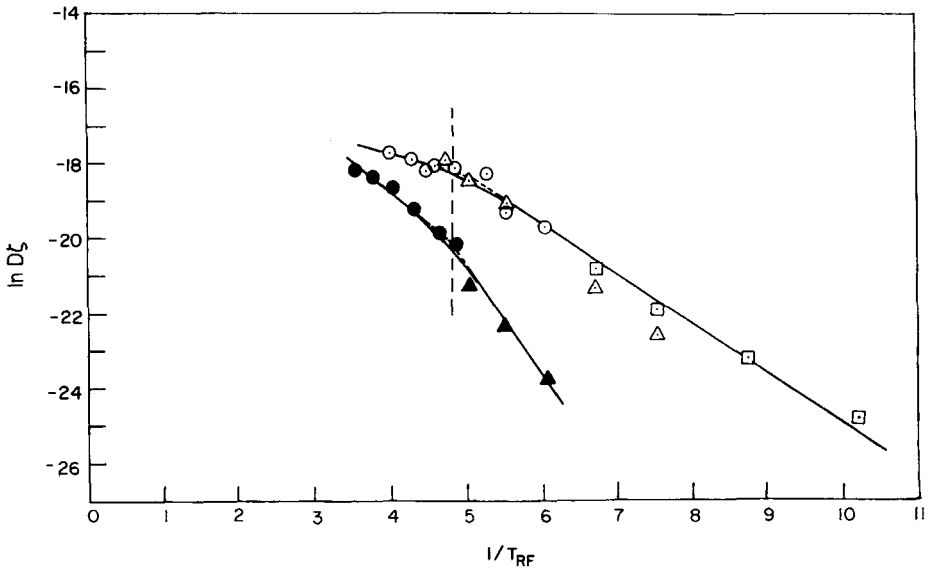
Fig. 6.   Ln $D\zeta$ versus $1/T_{RF}$. (a) Toluene in PS: ($\odot$) this study; ($\triangle$) Ni (Ref. 31); ($\square$) Pawlisch and Laurence (Ref. 20). (b) Toluene in PVAc: ($\bullet$) this study; ($\blacktriangle$) Vrentas and co-workers (Ref. 32).

where

$$a = \ln D_o\zeta \qquad (19)$$

$$b = -\gamma\hat{V}_2^*\xi/K_{12}T_c \qquad (20)$$

$$c = -E/RT_c \qquad (21)$$

$$T_{RF} = (K_{22} + T - T_{g2})/T_c \qquad (22)$$

$$T_R = T/T_c \qquad (23)$$

Using the experimental data (see Table III) obtained in this study, plots of ln $D\zeta$ versus $1/T_{RF}$ are presented in Figures 6 to 9 for toluene, benzene, ethylbenzene, and n-decane in PS and PVAc. It is seen in these figures that two linear regions appear to exist, separated by a certain critical value of $1/T_{RF}$. The critical value of $1/T_{RF}$ may be obtained by extrapolating the two linear regions as indicated by the dotted lines in Figures 6 to 9. It should be mentioned that actually there would be *no* discontinuity in the slope of ln $D\zeta$; the transition would be smooth as indicated in Figures 6 to 9. Plots of ln $D\zeta$ versus $1/T_{RF}$ are presented in Figure 10 for the four solutes in PS, including the literature data, and in Figure 11 for the four solutes in PVAc, also including the literature data. It should be mentioned that in the preparation of Figure 11 we have not included the benzene data of Ryskin,[7] displayed in Figure 7, in PVAc at temperatures above a critical value of $1/T_{RF}$. We believe that the accuracy of those data points is subject to serious question, because they seem to be exceedingly large, deviating considerably from the rest of the
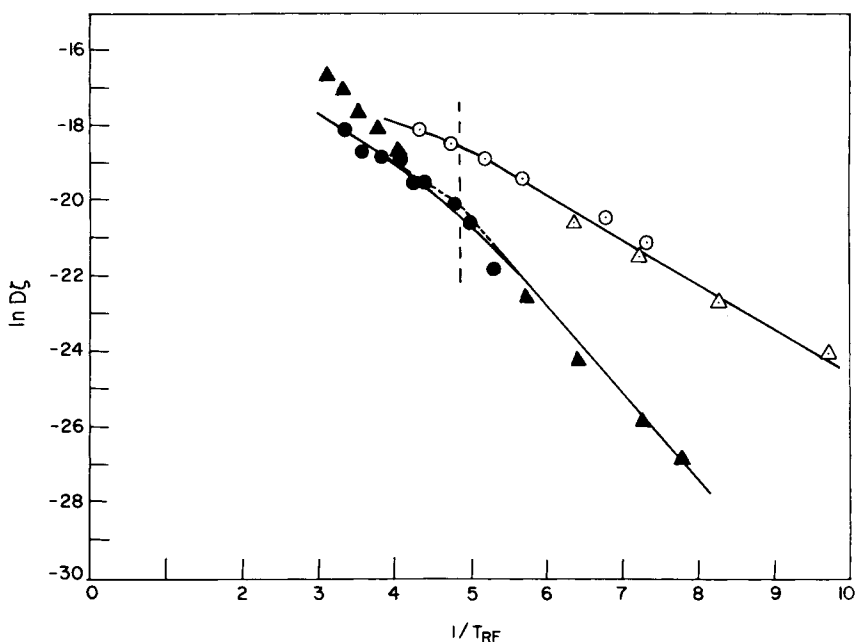
Fig. 7.   Ln $D\zeta$ versus $1/T_{RF}$. (a) Benzene in PS: ($\odot$) this study; ($\triangle$) Pawlisch and Laurence (Ref. 20). (b) Benzene in PVAc: ($\bullet$) this study; ($\blacktriangle$) Ryskin (Ref. 7).
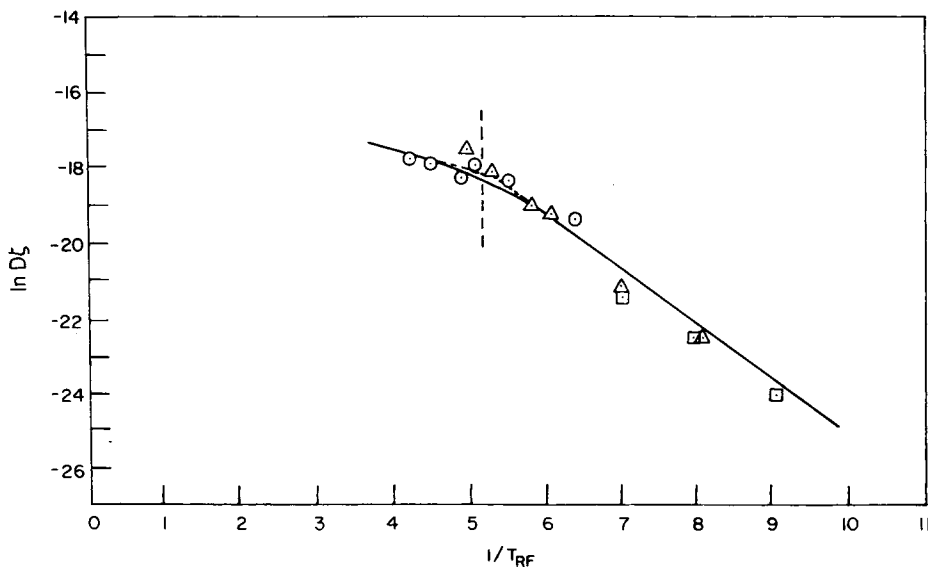

Fig. 8.   Ln $D\zeta$ versus $1/T_{RF}$ for ethylbenzene in PS: ($\odot$) this study; ($\triangle$) Ni (Ref. 31); ($\square$) Pawlisch and Laurence (Ref. 20).

data points. Note that T_{RF} defined by Eq. (22) represents a dimensionless temperature, hereafter referred to as *reduced* free volume temperature, and the slope in the ln $D\zeta$ versus $1/T_{RF}$ plots is represented by the dimensionless parameter b defined by Eq. (20).

The following observations may be made on the correlations shown in Figures 10 and 11: (1) ln $D\zeta$ versus $1/T_{RF}$ plots give two distinct linear
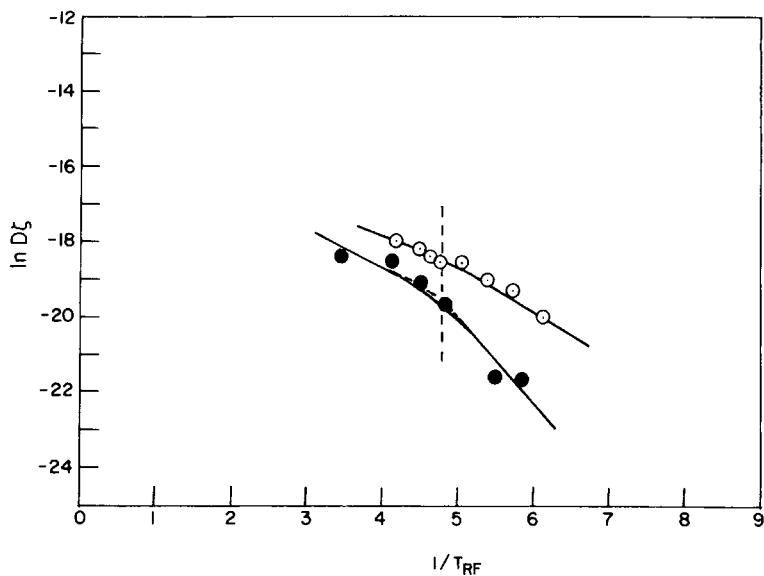
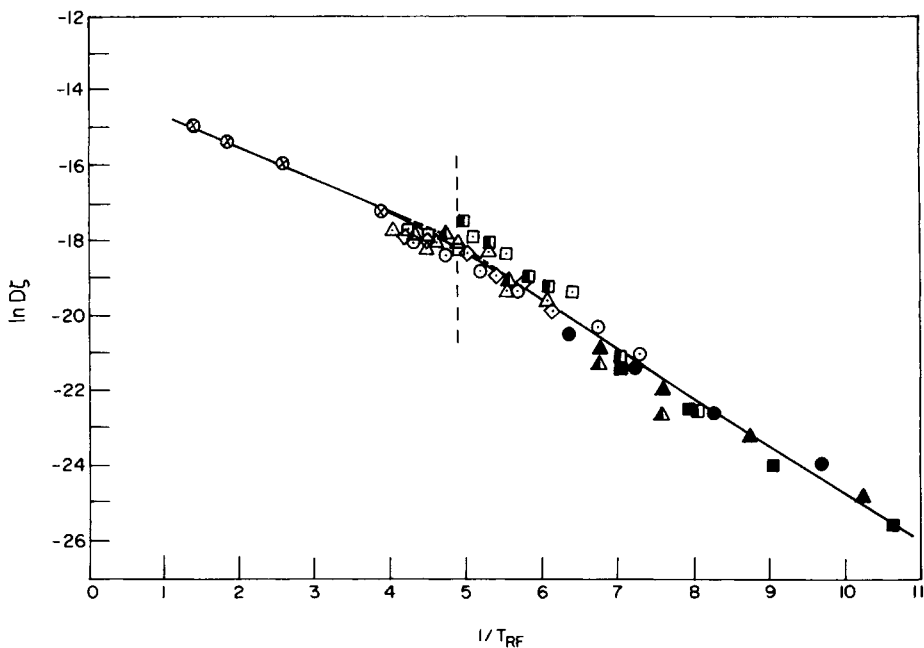Fig. 9.   Ln $D\zeta$ versus $1/T_{RF}$ for n-decane in: (○) PS; (●) PVAc.

Fig. 10.   Ln $D\zeta$ versus $1/T_{RF}$ for various solutes in PS. Symbols are the same as in Fig. 2.

regions that are separated at a critical value of $1/T_{RF}$. As mentioned above, the critical value of $1/T_{RF}$ may be obtained by extrapolating the two linear regions. In reality, there would be *no* discontinuity in the slope of ln $D\zeta$. The critical value of $1/T_{RF}$ appears to be independent of the type of solute and the structure of polymer; (2) the slope b in the ln $D\zeta$ versus $1/T_{RF}$ plots appears to be independent of the type of solute but dependent upon the
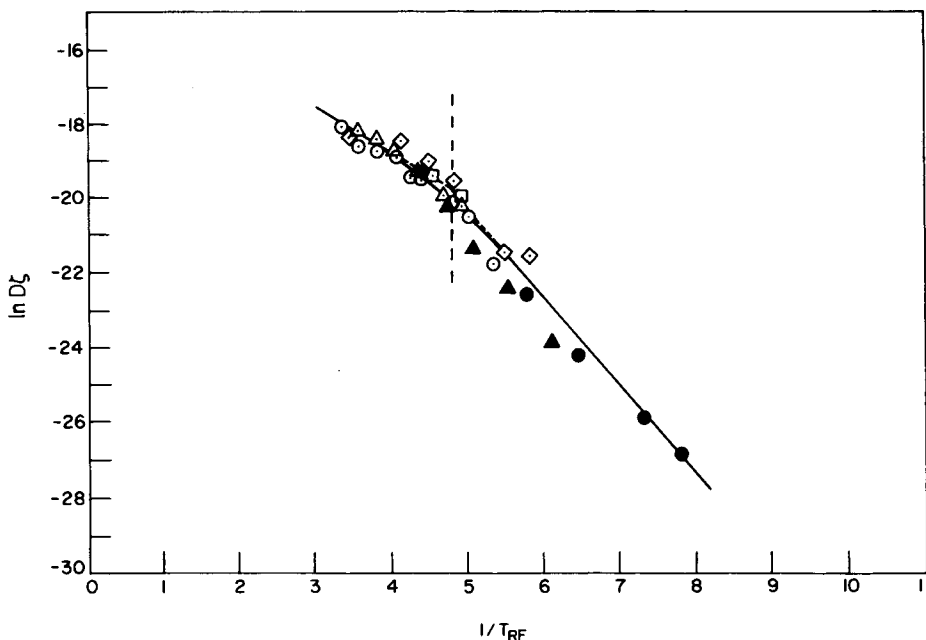
Fig. 11. Ln $D\zeta$ versus $1/T_{RF}$ for various solutes in PVAc. Symbols are the same as in Fig. 3.

structure of the polymer; (3) the diffusivity of methane in PS (see Fig. 10) can be correlated with the same degree of accuracy as other organic solutes, which was not possible with the Vrentas-Duda free volume correlation (see Fig. 4); (4) the slope b for PVAc is greater than that for PS both below and above the critical value of $1/T_{RF}$.

On the basis of the experimental results presented in Figures 6 to 9 for the four solutes investigated, and summarized in Figure 10 for PS and in Figure 11 for PVAc, we have obtained the critical value of $1/T_{RF}$ to be approximately 4.8. This value was determined by taking the average of the critical values of $1/T_{RF}$ for the individual solutes benzene, toluene, ethylbenzene, and n-decane. Using a similar procedure, we have obtained values of the slope b in the ln $D\zeta$ versus $1/T_{RF}$ plots to be -1.25 for PS and -2.54 for PVAc. The values of b determined in this study are very close to those that may be calculated using the literature data.[11]

It can therefore be concluded that the use of the reduced variables, ln $D\zeta$ and $1/T_{RF}$, shown in Figures 10 and 11, enables us to determine the upper limit of temperature, above which free volume theories are not entirely applicable to correlate the infinite dilution diffusion coefficient of solutes in molten polymers at elevated temperatures.

DISCUSSION

As pointed out above in reference to Figures 4 and 5, the Vrentas-Duda free volume theory enables us to obtain a correlation that considerably reduces the effect of the structure and the size of solute molecules on their infinite dilution diffusion coefficients in molten polymer, with the exception of the diffusion data available for methane. It should be noted, however, that free volume theories are applicable only up to a certain upper limit of temperature.

Note that the self-diffusion coefficient D of a low molecular weight liquid consisting of hard spheres is inversely related to the viscosity η by the Stokes-Einstein relation,[37]

$$D = kT/6\pi r\eta \qquad (24)$$

where k is the Boltzmann constant, T is absolute temperature, and r is the radius of the molecule. Based on viscosity measurements, it has been known for some time that the availability of free volume controls molecular transport up to temperatures about 100°C above the glass temperature of a polymer.[30] However, so far no experimental evidence has been reported about the upper limit of the temperature above which free volume theories may not be applicable to correlating the diffusivity of solutes of small molecular size in rubbery polymers.

Vrentas and Duda[27] noted that, as the temperature is increased, the specific hole free volume increases significantly, and the energy to overcome attractive forces assumes a more predominant role. The importance of the energy effect can be determined by calculating the fraction of the activation energy for diffusion which is needed to overcome intermolecular forces. As a matter of fact, Macedo and Litovitz[38] were the first to point out the importance of the consideration of energy effects, in addition to free volume effects, in correlating polymer viscosity data at high temperatures. The suggestion of Macedo and Litovitz was the basis for the inclusion of the term, $\exp(-E/RT)$, in Eq. (12).

Vrentas and Duda[39] noted that, in reference to Eq. (12), the total activation energy E_D may be given as

$$E_D = E + \left(\gamma\hat{V}_2^*\xi/K_{12}\right)RT^2/\left(K_{22} + T - T_{g2}\right)^2 \qquad (25)$$

in which the second term represents the contribution from free volume effects. Ju et al.[40] included energy effects in predicting the *mutual* diffusion coefficients, with the aid of Eq. (8), for *concentrated* polymer solutions at temperatures below 180°C for PS (using the quartz spring sorption balance) and below 65°C for PVAc (using the Cahn electrobalance). They obtained the following numerical values: $E = 8.07$ Kcal/g-mol and $D_o = 27.7 \times 10^{-7}$ cm^2/s for the PVAc/chloroform system, and $E = 4.80$ Kcal/g-mol and $D_o = 1.99 \times 10^{-7}$ cm^2/s for the PVAc/methanol system, using a nonlinear regression analysis based on Eq. (8).

In plotting their data with the aid of Eq. (13), the highest temperature available was 178°C in the study of Duda et al.[41] for the PS-ethylbenzene and PS-toluene systems. According to our results (for example, see Figs. 6 through 10), this temperature still lies in the lower linear region in the ln $D\xi$ versus $1/T_{RF}$ plots. The results of this study indicate that, at higher temperatures, energy effects would be observed, requiring non-zero values of E.

It can be seen from Figures 6 through 11 that, at temperatures lower than a certain critical value (i.e., at values of $1/T_{RF}$ larger than 4.8), free volume effects are predominant over energy effects. On the other hand, energy effects play an important role at temperatures higher than the critical value (i.e., at values of $1/T_{RF}$ smaller than 4.8). This has prompted us to plot ln $D\xi$ −
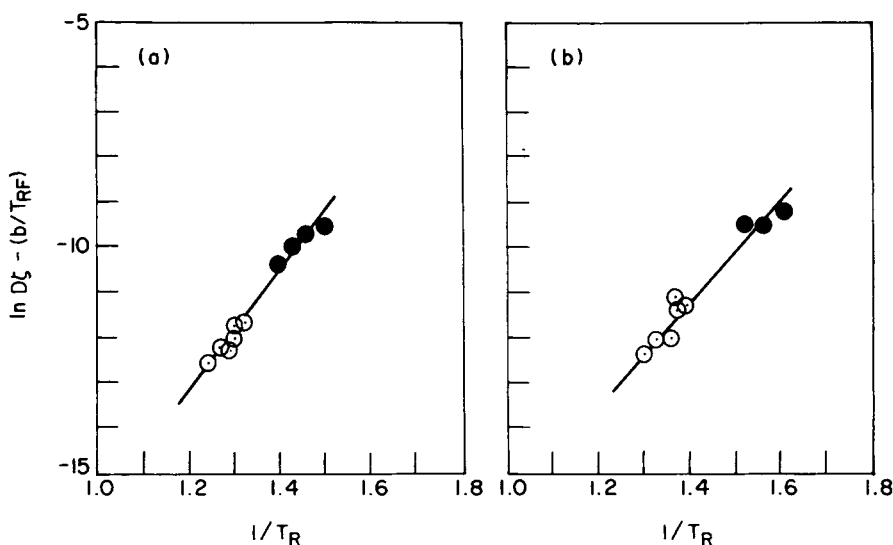
Fig. 12. Ln $D\zeta - (b/T_{RF})$ versus $1/T_R$ for: (a) benzene in PS ($\odot$) and in PVAc ($\bullet$); (b) n-decane in PS ($\odot$) and in PVAc ($\bullet$).

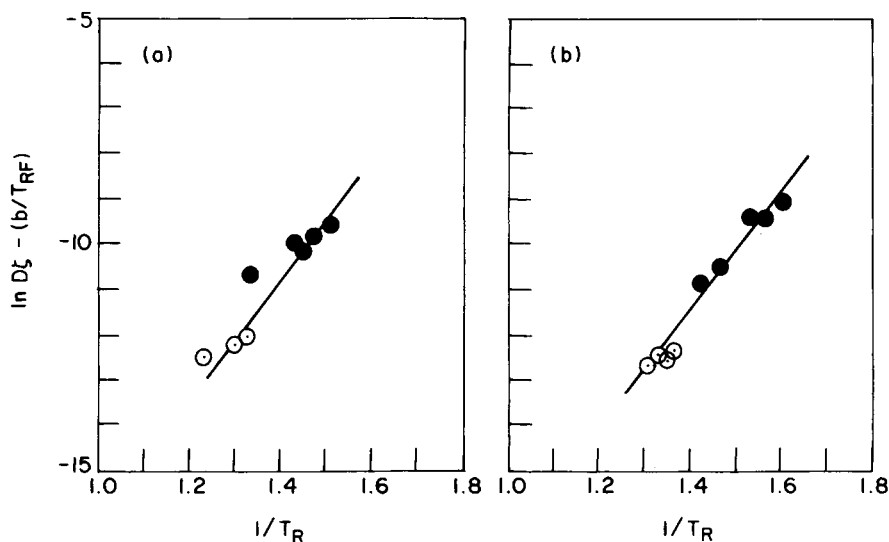Fig. 13. Ln $\zeta - (b/T_{RF})$ versus $1/T_R$ for: (a) toluene in PS ($\odot$) and in PVAc ($\bullet$); (b) ethylbenzene in PS ($\odot$) and in PVAc ($\bullet$).

(b/T_{RF}) against the reciprocal of the *reduced* temperature $(1/T_R)$, with the aid of Eq. (18), at temperatures greater than the critical value. The results are given in Figures 12 and 13. It should be noted that ln $D\zeta - (b/T_{RF})$ represents the difference between the actually measured values of diffusivity (ln $D\zeta$) and the values of diffusivity (b/T_{RF}) obtained from the extrapolation of the lower linear region in the ln $D\zeta$ versus $1/T_{RF}$ plots to temperatures above the critical value.

TABLE IV
Numerical Values of Energy Parameter E^a for Solutes in Polystyrene and Poly(vinyl Acetate)

Solute	a	c	E (Kcal/mol)
Benzene	-26.958	11.649	-12.96
Toluene	-29.331	13.349	-15.64
Ethylbenzene	-26.163	10.659	-13.02
n-Decane	-31.134	13.973	-17.09

^{a}Obtained from the slope c of the $\ln D_\zeta^* - (b/T_{RF})$ versus $1/T_R$ plots, in which c is defined by Eq. (21), i.e., $E = -cRT_c$.

It is seen, in Figures 12 and 13, that plots of $\ln D_\zeta^* - (b/T_{RF})$ versus $1/T_R$ yield a linear correlation which appears to be independent of the structure of polymer, and that the slope of such plots varies with the type of solute. With the aid of Eq. (18), the numerical values of the energy parameter E and the constant a obtained from Figures 12 and 13 are listed in Table IV. It should be pointed out that values of E have been reported to be close to zero (approximately ± 1 Kcal/mol) except for highly polar fluids or solutes of small molecules in PS and PVAc, at temperatures that are not far away from T_g.[32] It is seen in Table IV, however, that values of E obtained in this study are large enough to be of physical significance. This means that the energy term c/T_R in Eq. (18) becomes important as the temperature is increased above a certain critical value (i.e., below a certain critical value of $1/T_{RF}$).

At this juncture, it seems worth noting the temperature dependence of the self-diffusion coefficient of organic solvents. Dullien and Ertl[35,36] have investigated the temperature dependence of the self-diffusion coefficient of small molecules, and have successfully fitted their data to the following dimensionless expression:

$$\ln D_\zeta^* = a_2 + c_2/T_R \qquad (26)$$

with an average error between 1.0 and 4.0% in the range of temperature $0.3 < T_R < 0.7$. Note that Eq. (26) is a special case of Eq. (18) when free volume effects become negligibly small compared to energy effects [i.e., when $b = 0$ in Eq. (18)].

Plots of $\ln D_\zeta^*$ versus $1/T_R$ are given in Figure 14 for benzene in PS and PVAc. For comparison purposes, the self-diffusion coefficient of benzene reported in the literature[36] is also given in Figure 14. It is of great interest to observe in Figure 14 that values of D_ζ^* for benzene in PS and PVAc approach the value of the self-diffusion coefficient of benzene as the temperature is increased to a value which is much higher than a certain critical value. This again reinforces the conclusion, drawn above, that the contributions of the solute (i.e., energy effects) are important to the diffusivity of solutes in molten polymers at temperatures above a certain critical value, approximately 80°C above the glass transition temperature of the polymer.

In order to apply the generalized relationships in conjunction with gas chromatographic measurements, the results of this study indicate that, for values of $1/T_{RF}$ larger than the critical value, Eq. (18) should be expressed in
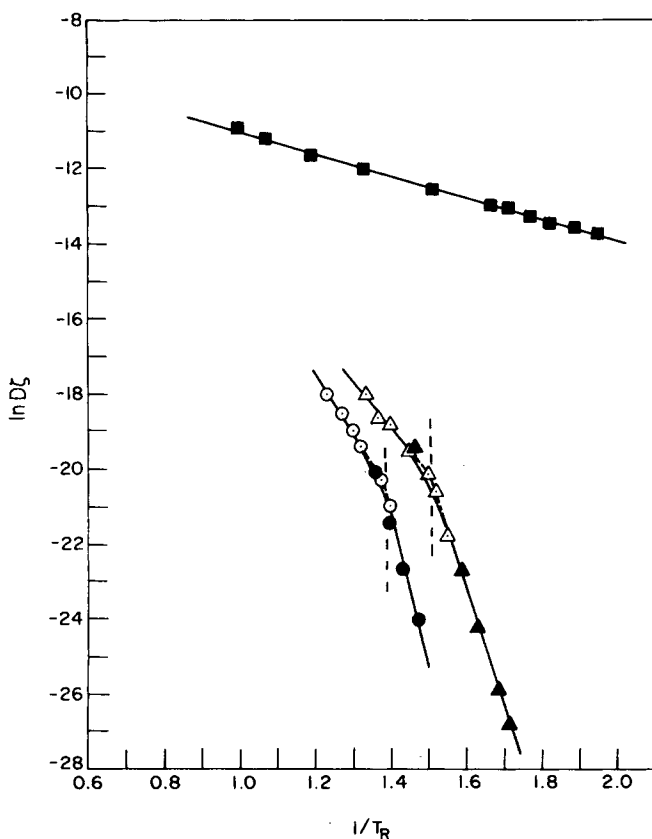
Fig. 14. Ln $D\zeta$ versus $1/T_R$. (a) Benzene in PS: (○) this study; (●) Pawlisch and Laurence (Ref. 20). (b) Benzene in PVAc; (△) this study; (▲) Ryskin (Ref. 7). (c) (■) self-diffusion of benzene (Ref. 36).

a form similar to Eq. (13) as

$$\ln D\zeta = \alpha + b/T_{RF} \tag{27}$$

where b is approximately a constant for a polymer in this free volume region, independent of the solutes investigated. While energy effects are undoubtedly present in this region, the data of this study do not appear to be sufficient for determining values of the constants a, b, and c of Eq. (18) that would be applicable to the entire range of $1/T_{RF}$ (both above and below the critical value). An analysis of the data for PS systems obtained in this study indicates that the constant α of Eq. (27) is approximately -12.15, independent of the solutes utilized. After the slope b is established for a polymer in the free volume region, the constants a and c of Eq. (18) can be determined from this relationship, by the use of experimental data for diffusion coefficients of the solute at values of $1/T_{RF}$ smaller than the critical value.

CONCLUDING REMARKS

It has been demonstrated above that the generalized Vrentas-Duda free-volume relationship that incorporates the solute critical temperature T_c and
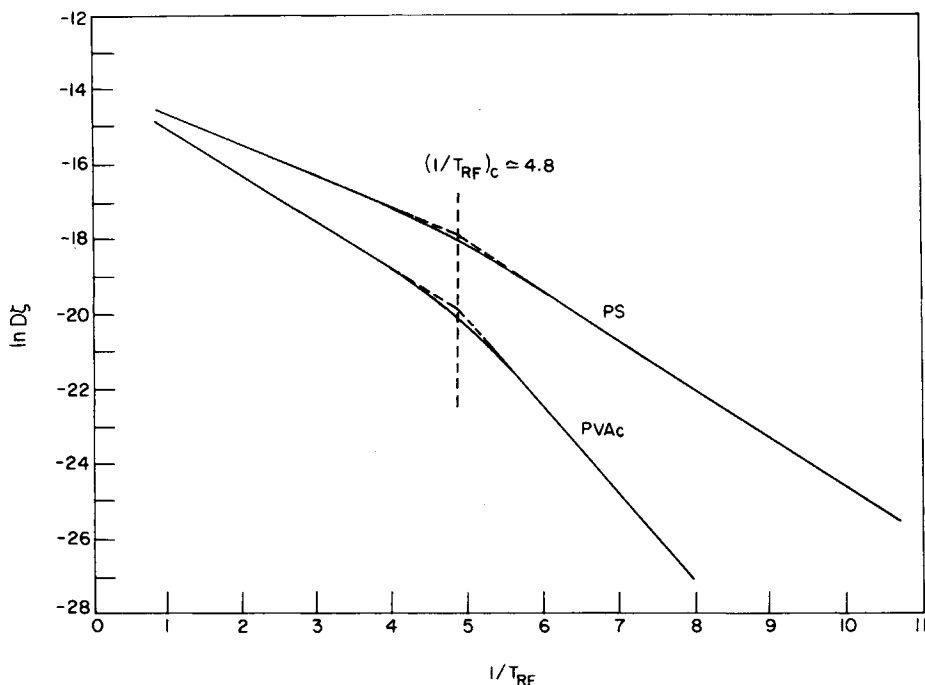
Fig. 15.   Ln $D\zeta$ versus $1/T_{RF}$ for PS and PVAc.

reduced diffusivity $D\zeta$ (which also includes the thermodynamic critical proper-
ties of the solute) gives rise to very useful correlations for the prediction of the
infinite dilution diffusion coefficients of volatile liquids in molten polymers,
over a wide range of temperatures above the T_g of the polymers. Within the
uncertainties of experimental data, the critical value of $1/T_{RF}$, approximately
4.8, appears to be independent of the structures of both solute and polymer, as
displayed in Figure 15. Such information is very useful for determining the
upper limit of the applicability of free volume theories in predicting the
infinite dilution diffusion coefficients of volatile liquids in molten polymer at
elevated temperatures. In the range of temperature where free-volume theo-
ries are entirely applicable, the slope of ln $D\zeta$ versus $1/T_{RF}$ plots seems to be
dependent only upon the structure of the polymer, independent of the
structure of the solute, as may be seen in Figure 15. This observation then will
permit us to predict the infinite dilution diffusion coefficients of solutes in this
region, other than those investigated here, in PS and PVAc, respectively. It
has been demonstrated above, also, that the extrapolation of the lower linear
region in the ln $D\zeta$ versus $1/T_{RF}$ plots to temperatures above the critical
value of T_{RF} (or below the critical value of $1/T_{RF}$) will result in significant
overestimates of diffusion coefficients of volatile liquids in molten polymers.

The use of IGC with a packed column, in conjunction with a generalized
Vrentas-Duda free volume relationship, appears to be promising for correlat-
ing and, also, for predicting infinite dilution diffusion coefficients of volatile
liquids in rubbery polymers at elevated temperatures. The IGC method makes
use of the van Deemter equation, which contains a geometric factor q,
appearing in Eq. (2), accounting for the nonuniformity of the liquid film in the

packed column. Since the value of q depends on the state of the packing of glass beads used, it must be determined, in general, after comparing the data obtained with IGC with another independent method, such as the sorption method. In this sense, the IGC method may be considered as an indirect method. However, once the value of q is determined, the IGC method can generate data very rapidly, whereas the sorption method, in general, is very time consuming, because one must wait a very long period for the system to reach equilibrium, especially when dealing with very viscous molten polymers. It should be pointed out that, at present, the IGC method can generate diffusion coefficient data of volatile liquids only at infinite dilution in rubbery polymers, and therefore its application is limited to the situations where the diffusion of *traces* of organic solutes or gases in molten polymer might be of practical interest, such as in the diffusion-controlled polymer devolatilization process.

For the packed columns prepared in this study with PS and PVAc, the constant q in Eq. (2) is approximately 1/6. This behavior indicates a high degree of nonuniformity for the liquid films on the glass beads. Further studies are required to confirm the generality of these results.

In the present investigation, we have used several sizes of glass beads (0.3, 0.5, 0.6, and 1.0 mm in diameters), depending on the system temperature and the polymer/solute pair chosen. We have found that, in order to obtain reliable data, as judged by the slope of plots of plate height versus linear velocity, larger glass beads were required as the system temperature was increased. However, the largest glass beads allowed for use is determined by the limiting value of the ratio of column diameter to bead diameter that ensures minimum wall effects. This has thus prevented us from investigating the diffusivity of solutes at higher temperatures than those reported in this study. This is a serious limitation of the IGC method.

More experimental studies, particularly for temperatures higher than those reported in this study, are needed to corroborate and/or extend the correlations presented here, using other experimental techniques. Also needed is a theoretical investigation that will enable one to predict the diffusivity of solutes in molten polymers in the range of temperature where both free volume effects and energy effects are important.

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