

Determination of Infinite Dilution Diffusion and Activity Coefficients of Solvents in Polystyrene by Inverse Gas Chromatography on a Capillary Column

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SYNOPSIS

Infinite dilution activity and diffusion coefficients of several solvents in polystyrene have been measured by inverse gas chromatography on a capillary column for temperatures between 110 and 170°C. Chromatographic data have been treated according to Khan's model, evaluating the contribution to the peak broadening due to radial and axial molecular diffusion in the mobile phase, radial diffusion in the stationary phase, and interfacial mass transfer resistance. Four capillary columns have been prepared with coating thickness ranging from 0.5 to 3.3 microns in order to determine the minimum thickness necessary to obtain reliable measurements of the diffusion coefficient of the solvent in the polymer in every possible experimental condition. Our experimental data are in considerable agreement with the data already available in the literature, obtained by static and chromatographic methods. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Knowledge and prevision of diffusion coefficients of small molecules in polymers are needed for the analysis of several problems involving polymer processing and applications. In many industrial processes like solvent devolatilization and bulk polymerization, solvent diffusion in the polymeric solution is the critical step, limiting the efficiency and the economy of the process.

Knowledge of small molecule diffusion in polymers is also important in residual monomer removal from polymeric material used for food packaging and in the study of controlled-release technology.

Most of the diffusion coefficients in the literature have been determined by sorption experiments.^{1,2} This experimental technique allows measurements of diffusion coefficients in a large range of solvent concentration, but experimental tests and data analysis are time-consuming.

Recently, inverse gas chromatography (IGC) has

been proposed as an alternative technique.³⁻⁵ It enables the rapid and simple measure of diffusion coefficients, but only for solvents at infinite dilution in molten polymers. Actually, there is a remarkable uncertainty regarding the accuracy of diffusion data obtained by IGC since a correct modeling of stationary-phase geometry in the column is difficult.⁵ According to Pawlisch,⁶ this difficulty can be overcome using capillary columns having a uniform distribution of the polymeric stationary phase on the wall. Columns with an elevated thickness of the stationary phase (experimentally not easy to obtain) have been used by Pawlisch.

The data analysis carried out by Pawlisch was based on Macris' model⁷ for the capillary chromatography. Macris' model, starting from the more general but more complicated Khan's model,⁸ correlates the second central moment of the chromatographic peak with the infinite dilution diffusion coefficient of a solute in stationary phase and neglects the peak broadening due to interfacial mass transfer resistance and radial and axial diffusion of solute in the mobile phase.

In our study, we investigated the applicability of Macris' model on a polystyrene-solvent system for

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a capillary column with film thickness ranging from 0.5 to 3.3 microns. The main purpose of our work was to estimate the contribution of different phenomena on the chromatographic peak broadening; their relative weights have been evaluated varying the flow rate, the temperature, and the film thickness. Moreover, we aimed to find the experimental conditions to work with capillary columns having a stationary phase thinner than those used by Pawlich and, then, easier to prepare.

THEORY

The IGC technique is based on partition of a volatile solute between the gaseous mobile phase and the polymeric stationary phase. The solute is injected at the column inlet and is transported by a gas carrier to a detector.

By retention time measurements, it is possible to determine thermodynamic data such as Henry constants, infinite dilution activity coefficients, and Flory-Huggins interaction parameters.⁹ From the shape of the chromatographic peak, it is possible to obtain information related to transport phenomena in the column.

Ideally, a probe injected into a chromatographic column should arrive at the detector as an infinitely sharp peak, after a time depending on the interaction between the vapor and the stationary phase. In reality, several factors contribute to the peak broadening:

- instrumental factors (injection time, detector dead volume);
- thermodynamic factors (not linear partition isotherms); and
- transport factors (i.e., vapor diffusion in stationary and gas phases).

According to Van Deemter's model, transport factors are related to column characteristics by the equation

$$HEPT = A + B/V + C \cdot V \quad (1)$$

where *HEPT* is the height equivalent to one theoretical plate; *V*, the flow rate; and *A*, the eddy diffusion (and is null for capillary columns¹⁰); *B* depends on the axial diffusion in the gas phase and on the tortuosity or structural factors in the column, and *C* depends, among others, on probe diffusion in the liquid phase and on transport processes within the gas phase in the radial direction.

The *HEPT* is determined from the eluted peak by the relation

$$HEPT = L \cdot \sigma_t^2 / t_r^2 \quad (2)$$

where *L* is the column length; σ_t^2 the peak variance, and *t_r*, the retention time.

In eq. (1), if elevated flow rates are used, the term *B/V* becomes negligible and a plot of *H* vs. *V* should be a linear plot with slope *C*. The knowledge of *C* enables the calculation of the probe diffusion coefficient in the stationary phase by the equation

$$C = (8/\pi^2) \cdot (\tau^2/D_p) \cdot (K/\epsilon) \cdot (1 + K/\epsilon)^{-2} \quad (3)$$

where *D_p* is the diffusion coefficient in the stationary phase; τ , the film thickness; *K*, the partition coefficient, and ϵ , the ratio of the stationary-phase volume to the gas-phase volume.

It is important to note that this method is valid only when

- the whole mass transfer resistance is due to diffusion in the stationary phase;
- stationary phase support is spherical and uniform;
- film thickness is constant and uniform; and
- instrumental and thermodynamic contributions to peak broadening are negligible.

Usually, in packed columns, the liquid film distribution is not uniform. In this case, the constant $8/\pi^2$ of eq. (3) must be replaced by an empirical geometric factor *q*, and τ , by the film thickness at its deepest point. The geometric factor can be obtained eluting a probe whose diffusion coefficient is already known. Therefore, IGC on a packed column is an indirect method for measuring the infinite dilution diffusion coefficient.

This technique is useful in determining the relative diffusion coefficient of different solvents in a polymer. If measurements of peak broadening are carried out for different probes using the same column, the diffusion coefficient can be obtained with no information about the column geometry: The geometric parameter is the same in each experiment and disappears in calculating the ratio.

In the particular case of a capillary column, it is possible to obtain a uniform distribution of the stationary phase on the tube wall using the static coating technique. This makes it easier to model the dispersion of a solute slug flowing through a capillary column. In fact, several models for the capillary

chromatography can be found in the literature. Khan's and Macris' models are the most interesting for our purpose.

According to Khan's model, there are four kinetic phenomena that contribute to the peak broadening:

- (a) radial diffusion of the solute in the stationary phase;
- (b) radial diffusion of the solute in the mobile phase;
- (c) axial diffusion of the solute in the mobile phase; and
- (d) interfacial mass transfer resistance.

The basic equations of Khan's model are

$$\mu_1 = \left(1 + \frac{2 \cdot K \cdot \tau}{R}\right) \cdot t_c \quad (4)$$

$$\begin{aligned} \mu_2^* &= \frac{\int_0^\infty (t - \mu_1)^2 \cdot C(t) dt}{\int_0^\infty C(t) dt} \\ &= \left[\frac{4 \cdot \tau^3 \cdot K}{3 \cdot R \cdot D_p} \cdot \frac{1}{t_c} + \frac{2 \cdot D_g \cdot (1 + K')^2}{L^2} \right] \cdot t_c \\ &\quad + \frac{(1 + 6K' + 11K'^2) \cdot R^2}{24 \cdot D_g} \\ &\quad + \frac{4 \cdot K \cdot \tau^2}{R \cdot K_d} \cdot \frac{1}{t_c} \cdot t_c^2 \\ &= \left[a \cdot \frac{1}{t_c} + b \cdot t_c + c + d \cdot \frac{1}{t_c} \right] \cdot t_c^2 \quad (5) \end{aligned}$$

where $K' = (2K\tau/R)$; t_c is the residence time of the carrier gas; μ_1 , the first statistical moment (mean retention time); μ_2^* , the second central statistical moment (variance of the distribution); $C(t)$, the solute concentration in the gas phase at time t ; D_g , the gas-phase diffusion coefficient; R , the column inner radius; and K_d an interfacial desorption rate coefficient.

The terms contributing to the peak broadening depend on the carrier flow rate ($1/t_c$), on column geometry, on the stationary-phase thickness, and on the probe diffusion coefficient in the polymeric and mobile phases. Therefore, the relative weight of the addends in eq. (5) is different depending on the experimental conditions and on the stationary-phase solute system.

For the system studied by Khan (stationary-phase chloroform; probe: acetone; column inner ra-

dius: 0.02 cm; film thickness: 0.2 micron), the interfacial mass transfer resistance gave the most important contribution to the peak broadening, and the contribution of the probe diffusion in the stationary phase was negligible.

According to Macris, Khan's model can be simplified if the stationary phase is a polymer because, in this case, the interfacial resistance and the radial diffusion are negligible. In fact, the diffusion coefficient in a polymeric phase can be 6-8 orders of magnitude smaller than that in the gas phase. In this case, eq. (5) can be simplified:

$$\mu_2^* = \left[\frac{4 \cdot \tau^3 \cdot K}{3 \cdot R \cdot t_c \cdot D_p} + \frac{2 \cdot D_g \cdot t_c}{L^2} \right] \times (1 + 2 \cdot \tau \cdot K/R)^2 \cdot t_c^2 \quad (6)$$

For elevated film thickness, the second term in eq. (6) becomes negligible and D_p can be calculated knowing only film thickness, inner radius, and retention time of a nonadsorbed material (i.e., methane):

$$\mu_2^* = \frac{4 \cdot \tau^3 \cdot K}{3 \cdot R \cdot D_p} \cdot t_c \quad (7)$$

EXPERIMENTAL

Preparation of Coated Columns

Five columns have been used in this study. Their characteristics are shown in Table I.

The polymeric film was applied by the static coating technique. By this method, in fact, a coating of uniform and known thickness is allowed. The final film thickness was determined by the concentration of the coating solution:

$$\tau = \frac{R \cdot p}{200} \quad (8)$$

where τ is the film thickness (microns); R , the column inner radius (microns); and p , the volume percent of the polymer in the solution.

The columns were filled with the coating solution and then carefully sealed at one end with a silicone rubber-glass plug. This is the critical step in the experiment, because it is very important to avoid air bubbles in the column, especially at the sealed end. The columns were placed in a water bath and connected to the vacuum via the open end until the complete evaporation of the coating solution was

Table I Capillary Columns Characteristics

Column	Inner Radius (mm)	Length (m)	Coating Solvent	Film Thickness (Microns)
A	0.160	10	CH ₂ Cl ₂	0.43
B	0.166	12	CH ₂ Cl ₂	1.12
C	0.166	13	CH ₂ Cl ₂	2.27
D	0.166	13	CH ₂ Cl ₂	0.46
E	0.166	8	CH ₂ Cl ₂ /pentane	3.35

obtained. Then, they were conditioned in a chromatographic oven under helium flow, increasing the temperature by 0.5°C/min until complete removal of the solvent. Only the columns having a perfectly uniform and smooth coating were used for the determination of the diffusion coefficient.

Measurement of the Column Inner Radius

The columns were obtained from a 100 m-long glass capillary tube, cut to the required length. From every cut, a coil was taken. Each coil was weighted, filled with mercury, and weighted again and, finally, its length measured. From these measurements, the average inner diameter (reported in Table I) was obtained. The variance on the whole set of measurements was 0.0036 micron.

Materials and Equipment

Polystyrene (Edistir N 1280) was supplied by Enichem Polimeri (Mantova, Italy). Its weight-average molecular weight (M_w) and its glass transition temperature were 300,000 and 98°C, respectively. All the solvents used were Carlo Erba RP and they were used without further purification.

The measurements were performed on a Carlo Erba Fractovap 4160 gas chromatograph, equipped with a flame-ionization detector (FID) and a splitless injector. The split ratio was 100 : 3.

Helium was used as the carrier gas, and flow rates were measured by a common soap-bubble flowmeter at the detector outlet. Flow rates in the column ranged from 0.5 to 6 mL/min.

Solvents were injected as vapors, sampling the head space of the liquid kept at room temperature using a 50 μ L Hamilton syringe. Vapor amounts from 10 to 50 μ L were injected in order to check that the sample size does not affect the measure. Three different flow rates were tested for each sample and temperature. The detector output was mon-

itored with a Hewlett-Packard integrator, Model 3393 A.

To obtain the first-order moment data, the raw output signal was transferred to a personal computer HP Vectra ES. The raw signal data were corrected for the base-line offset and then the mean retention time (μ_1), the second central moment of the elution curve (μ_2^*), and the peak area were calculated using numerical integration.

RESULTS AND DISCUSSION

We started data analysis according to Khan's model.⁸ We first estimated the peak-broadening contributions caused by the different diffusion phenomena by data of diffusivity in the polymer phase D_p and in the gas phase D_g , taken from the literature.^{6,11}

Khan's model shows that the different contributions to peak broadening are additive [eq. (5)]; in Table II, their values, expressed as μ_2^*/t_c^2 , are reported for the system polystyrene-ethylbenzene at 150°C in columns of different polymer thicknesses and at various carrier flows. It is evident that the radial diffusion in the gas-phase [term (b)] has always a very slight effect on the peak width even for the smallest polymer thickness, so we can neglect it.

The probe axial diffusion in the carrier gas [term (c)] has a more critical behavior. Its influence compared to the stationary-phase diffusion term (a) is shown in Figure 1 vs. the stationary phase thickness τ , for two carrier gas rates. The diagram shows that the term (c) becomes negligible only for polymer thickness greater than a value depending on the carrier gas velocity and on the column geometry [eq. (4)]. In our columns at 150°C, term (c) is lower than 5% of term (a) for stationary-phase thicknesses greater than 1.2 and 3 microns, at carrier gas residence time (t_c) of 1 and 3 min, respectively (Fig. 1 and Table II).

Table II Contributions to the Peak Broadening at 150°C

Column	Film Thickness (Microns)	t_c (Min)	Term (a) *10E6	Term (b) *10E6	Term (c) *10E6
A	0.43	1	207	1.2	66
B	1.12	1	3,599	3.8	116
C	2.27	1	29,967	11.1	230
E	3.35	1	96,500	21.5	373
A	0.43	2	104	0.6	132
B	1.12	2	1,800	1.9	231
C	2.27	2	14,984	5.5	460
E	3.35	2	48,250	10.8	746
A	0.43	3	69	0.4	198
B	1.12	3	1,200	1.3	347
C	2.27	3	9,989	3.7	690
E	3.35	3	32,167	7.2	1119

Since our columns have polymer film thicknesses ranging from 0.5 to 3.3 μm , we have always taken into account the axial diffusion in the gas phase to obtain suitable data of diffusivity in the stationary phase. This is possible by carrying out experiments at several flows and plotting measured μ_2^*/t_c vs. $1/t_c^2$; the resulting diagram should show a straight line. In fact, by neglecting the radial diffusion in the gas phase, eq. (4) can be turned into the following:

$$\frac{\mu_2^*}{t_c^3} = \frac{2 \cdot D_g \cdot (1 + K')^2}{L^2} + \left(\frac{4 \cdot \tau^3 \cdot K}{3 \cdot R \cdot D_p} + \frac{4 \cdot K \cdot \tau^2}{R \cdot K_d} \right) \cdot \frac{1}{t_c^2} \quad (9)$$

The intercept (q) includes the contribution due to the radial diffusion in the gas phase, D_g , and the slope (m) includes both the interfacial resistance, K_d , and the polymer diffusivity, D_p . In Figure 2, experimental data of μ_2^*/t_c are plotted for 1 and 2 μm stationary-phase thickness columns.

The interfacial resistance [term (d) in eq. (5)] is the last term influencing the diffusion coefficients calculation in the polymer phase. An *a priori* evaluation of this term for our system is difficult⁸; an estimate of its contribution to gas chromatographic data can be made through experiments on columns of different polymer thicknesses.

Khan's model predicts that the broadening due to the interfacial resistance, and the diffusion in the stationary phase have different behavior in respect to the variation of the film thickness, because they depend on the second power of the film thickness and on the third, respectively. As m is the slope of

the straight line in eq. (9), plotting the ratio m/τ^3 vs. the reciprocal film thickness $1/\tau$, we should have a straight line again. The slope now represents the interfacial resistance, and the intercept, the diffusivity:

$$\frac{m}{\tau^3} = \frac{4 \cdot K}{R \cdot D_p} + \frac{4 \cdot K}{R \cdot K_d} \cdot \frac{1}{\tau} \quad (10)$$

Such a diagram is shown in Figure 3 for columns B, C, and E and temperature between 110 and 170°C.

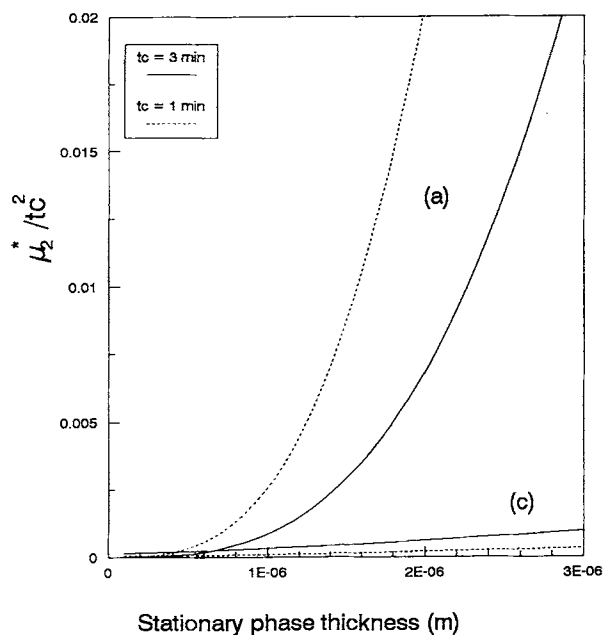


Figure 1 Peak broadening caused by the axial diffusion in the carrier (c) and by the diffusion in the polymer (a), at two different carrier velocities.

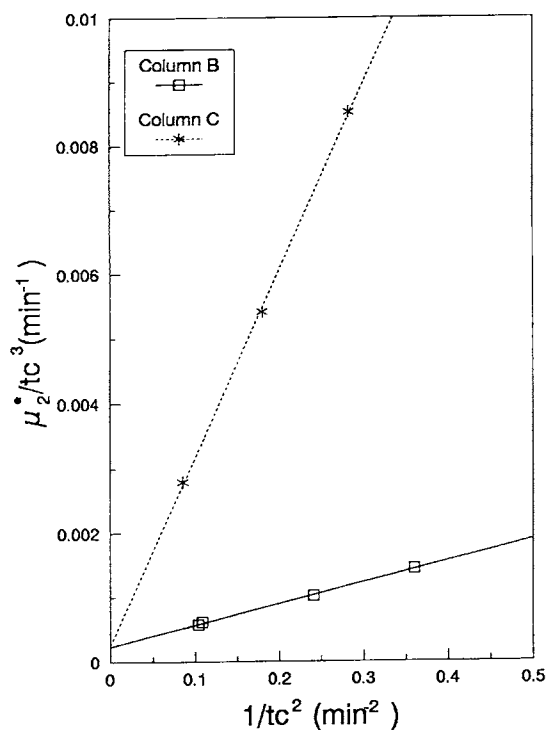


Figure 2 Experimental data of μ_2/t_c^3 vs. $1/t_c^2$ for ethylbenzene in polystyrene at 150°C.

The reported values show that there is not an appreciable dependence of m/τ^3 on $1/\tau$; the deviations from horizontal lines, evident at the extreme temperatures, would carry to a negative value of the interfacial resistance, so they must preferentially be

related to experimental errors and uncertainty in determination of a high skewed peak end. The interfacial resistance does not play an important role in this system.

Ethylbenzene diffusion coefficients obtained on the various columns are reported in Table III. The results agree very well in the whole range of stationary phase thickness; they also agree with literature data obtained by static and chromatographic methods.

When the polymer thickness in the column is lower than 1 μm , the obtained data are reliable only at the temperature of 110°C; with these columns, at higher temperatures, peak broadening due to physical phenomena is very small and the spreading caused by instrumental apparatus and data acquisition is not negligible.

Diffusion coefficients relative to other solvents are presented in Table IV. The dependence of $\log D_p$ vs. T^{-1} is not linear: The slope decreases as temperature increases, as expected by the free-volume theory.¹² In the same class of compounds, diffusivities are greater for molecules of smaller dimensions, as expected (Fig. 4).

Data obtained at 110°C are reliable for aromatic solvents only, whereas for the aliphatic ones, this temperature is clearly too close to the polymer T_g to assure that the retention mechanism is not affected by surface-adsorption phenomena. It is well known¹³ that an Arrhenius plot of the specific retention volume V_g^0 does not provide straight lines in the region of phase transitions. Nevertheless, the

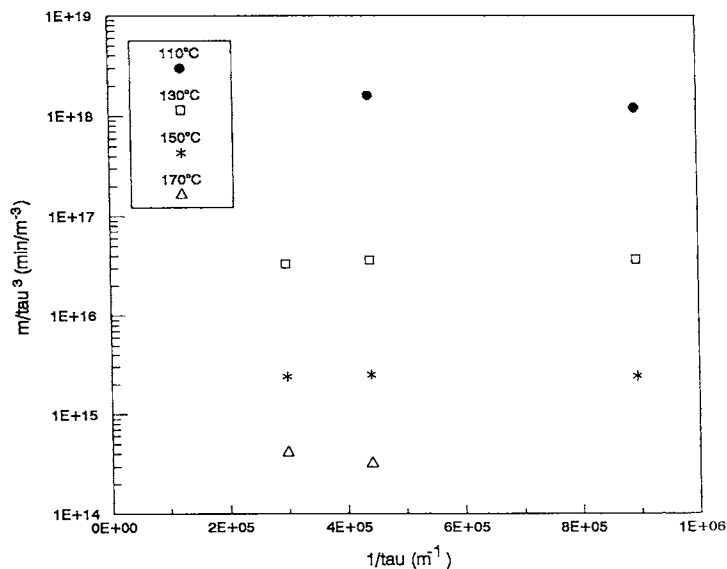


Figure 3 Influence of the interfacial resistance on the experimental diffusivities.

Table III Diffusion Coefficients of Ethylbenzene in Columns of Different Film Thicknesses

Column	Log D_p 110°C	Log D_p 130°C	Log D_p 150°C	Log D_p 170°C
B	-9.86	-8.59	-7.62	
C	-9.96	-8.57	-7.62	-6.91
E		-8.50	-7.57	-6.97

specific retention volumes of the aromatic solvents show only a very slight deviation from the linearity. This is probably due to the higher affinity to the polymer under discussion that causes the prevalence of the bulk sorption on the surface adsorption even at temperatures close to the polymer T_g .¹⁴ Experimental V_g^0 behavior vs. temperature of both aromatic and aliphatic solvents is shown in Figure 5. Specific retention volume has been obtained from thermodynamic partition coefficient K [eq. (4)] through the following equation:

$$V_g^0 = \frac{273.2 \cdot K}{T \cdot \rho_p} \quad (11)$$

where T is the temperature of the column, and ρ_p , the density of the polymer. Infinite dilution activity coefficients Ω^∞ (based on mass fraction as suggested by Patterson et al.¹⁵) are finally obtained by the following:

$$\ln \Omega^\infty = \ln \frac{273.2 \cdot Rg}{p_1^0 \cdot V_1^0 \cdot M_1} - \frac{p_1^0 \cdot (B_{11} - V_1)}{Rg \cdot T} \quad (12)$$

where Rg is the ideal gas constant; M_1 , the molecular weight; p_1 , the vapor pressure; B_{11} , the second virial coefficient; and V_1 , the liquid molar volume, all referred to the probe. The measured activity coefficients are presented in Table V; the difference between aromatic and aliphatic compounds reflects their difference in the affinity to the polymer. The experimental data for the aromatics are in good agreement with those presented in the literature.⁶

CONCLUSION

Inverse gas chromatography on a capillary column is a good technique for measurements of diffusion and activity coefficients of solvents in polymers at infinite dilution. Attention must be paid to the choice of experimental conditions (temperature and carrier flow rate) and column parameters (internal radius and stationary-phase thickness) in order to minimize unadvisable effects in diffusivity data.

Thermodynamic data are generally reliable at temperatures 30°C at least higher than T_g because

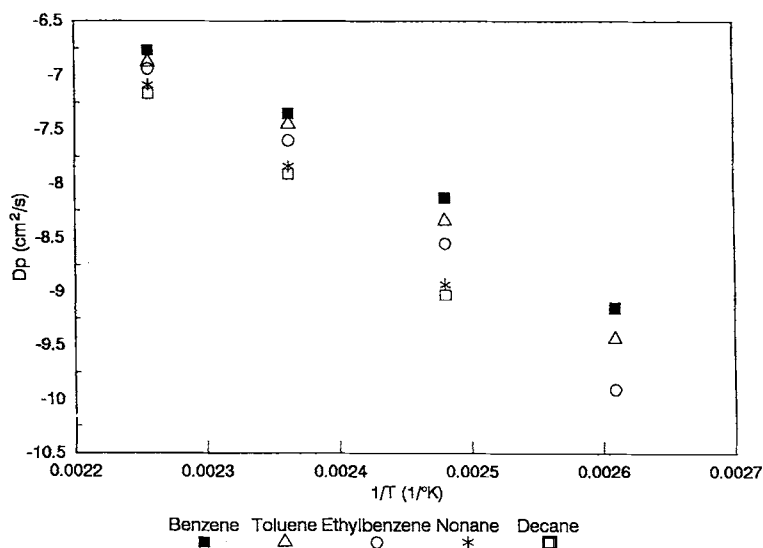


Figure 4 Temperature dependence of the infinite dilution diffusion coefficient.

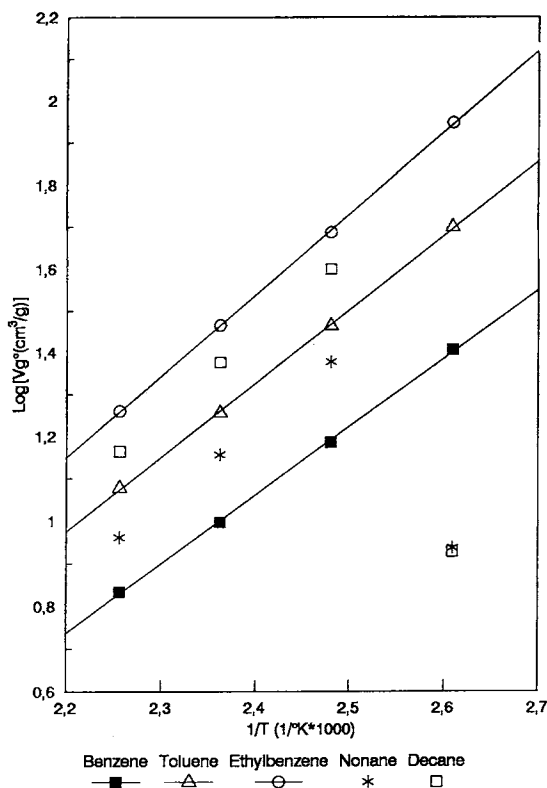


Figure 5 Temperature dependence of the specific retention volume.

of the influence of surface adsorption near the T_g . This limit may be lower for compounds with a great affinity for the polymer.

Table IV Diffusion Coefficients of Hydrocarbons in Polystyrene

Solute	Log (D_p)			
	110°C	130°C	150°C	170°C
Benzene	-9.15	-8.13	-7.35	-6.77
Toluene	-9.44	-8.34	-7.45	-6.88
Nonane		-8.93	-7.84	-7.09
Decane		-9.03	-7.91	-7.17

Table V Activity Coefficients of Hydrocarbons in Polystyrene

Solute	110°C	130°C	150°C	170°C
Benzene	5.13	5.24	5.50	5.65
Toluene	5.18	5.14	5.23	5.33
Ethylbenzene	5.26	5.20	5.14	5.20
Nonane		13.60	12.40	12.40
Decane		14.60	13.00	12.30

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