

Toluene Diffusion in Molten Polystyrene

INTRODUCTION

Although diffusion coefficients for polymer solutions are required in the analysis of many polymer formation and fabrication steps, there exist relatively few diffusivity data at the temperatures and concentrations of interest for these processes. A sorption apparatus has been developed¹ for the study of diffusion in polymer solutions over wide temperature and concentration ranges, and a comprehensive set of data has been reported² for the ethylbenzene–polystyrene system. Diffusivity data for other solvents in polystyrene are useful³ in the evaluation of theories describing penetrant diffusion in amorphous polymers. In this paper, we present data for the toluene–polystyrene system in the temperature range of 110–178°C and for concentrations as high as 80 wt-% toluene. The general features of the data are discussed, and diffusion of toluene in polystyrene is compared with previous studies involving diffusion of benzene⁴ and ethylbenzene² in polystyrene.

EXPERIMENTAL

The diffusivity data reported here were collected using a conventional quartz spring balance which was modified for high-temperature measurements. The apparatus and experimental procedure are described in detail elsewhere.^{1,2} Since the sorption apparatus was constructed to operate at solvent vapor pressures no higher than atmospheric, only a limited concentration range could be covered for experiments conducted at temperatures greater than 110°C. Experiments at these temperatures were terminated when the toluene vapor pressure was approximately 700 mm of mercury. For experiments carried out at temperatures of 110°C or lower, it is in principle possible to cover the entire concentration range without exceeding the pressure limitations of the apparatus. In practice, however, the concentration interval over which accurate data can be obtained is limited by the characteristics of the temperature controllers used on the apparatus.² With the particular apparatus utilized in this study, it was possible to cover nearly 80% of the weight fraction interval at 110°C.

The concentration range at each temperature was traversed using step-change sorption experiments, and diffusion coefficients were determined from the step-change experiments using a new method of analysis.⁵ With this method of analyzing sorption experiments, each experiment yields a value of the mutual diffusion coefficient at a known concentration. The data collected in this study are presented in Figures 1 and 2. The points in these figures represent the value of the diffusion coefficient calculated for each experiment, and the lines are simply visual aids. All of the experiments were carefully designed to avoid anomalous relaxation effects in the polymer–solvent system so that meaningful diffusion coefficients can be determined.^{6,7} The experiments were conducted using an additive-free commercial polystyrene with a weight-average molecular weight of 275,000.

RESULTS AND DISCUSSION

The data in Figures 1 and 2 clearly illustrate the strong concentration dependence of the diffusivity at low solvent mass fractions. The change in D , the mutual diffusion coefficient, with the mass or weight fraction of toluene is more pronounced at lower temperatures and at lower solvent concentrations. This behavior is typically observed in experiments involving the diffusion of penetrants in amorphous polymers above the glass transition temperature.^{2,8} Furthermore, these results are predicted by a new version of the free volume theory for polymer–solvent diffusion.^{9,10} From Figure 2 it is evident that D assumes a maximum value at a toluene weight fraction of approximately 0.30. Maxima in diffusivity–concentration curves have been observed by other investigators for polystyrene–solvent systems,^{2,11,12} and, again, this behavior has been predicted by free volume theory.^{9,10} At a comparable temperature, the maximum diffusivity for the toluene–polystyrene system appears to occur at a lower weight fraction than for the ethylbenzene–polystyrene system.

In Figure 3 the logarithm of D is plotted versus $1/T$ at three mass fractions of toluene to illustrate the dependence of the effective activation energy for diffusion on temperature and solvent mass

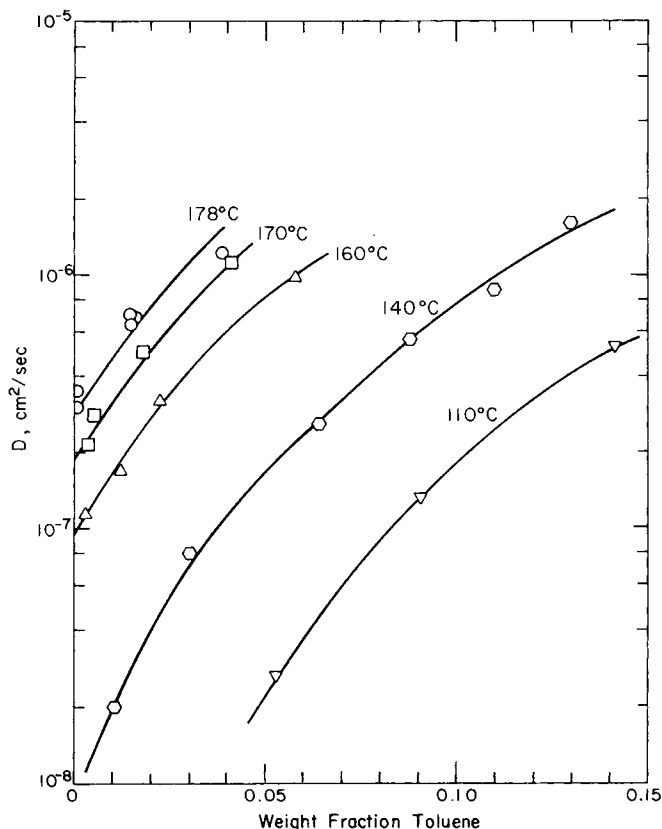


Fig. 1. Diffusivity data for the toluene-polystyrene system.

fraction ω_1 . In the limit of zero-solvent mass fraction, the effective activation energy decreases significantly as the temperature is increased. At the two higher toluene weight fractions, only a small temperature dependence of the activation energy is observed, and, furthermore, there is a significant decrease in the effective activation energy with increasing solvent concentration at a given temperature. A graph that illustrates the essential features of Figure 3 has been generated for the ethylbenzene-polystyrene system based on theoretical calculations using the equations of free volume theory.¹⁰

Since diffusivity data are now available for benzene,⁴ toluene, and ethylbenzene,² three successively larger aromatic hydrocarbons, it is of interest to see what effect the increasing size has on the diffusion process. The effect of solvent size on polymer-solvent diffusion is probably best examined by considering the temperature dependence of the mutual diffusion coefficient at zero solvent mass fraction.³ This temperature dependence can be described by the equation

$$\ln D = \ln D_{01} - \frac{\gamma \hat{V}_2^* \xi}{K_{12}(K_{22} + T - T_{g2})} \quad (1)$$

where D_{01} , $\gamma \hat{V}_2^* \xi / K_{12}$, and K_{22} are three parameters of free volume theory which are discussed elsewhere³ and where T_{g2} is the glass transition temperature of the polymer. This equation describes the self-diffusion of solvent molecules in the limit of pure polymer, and it is based on consideration of the probability that a fluctuation in local density will produce a hole of sufficient size so that a solvent molecule can perform a jump. The quantities K_{22} and $\gamma \hat{V}_2^* / K_{12}$ are simply related to the WLF constants of the pure polymer, D_{01} is a temperature-independent preexponential factor, and ξ is the ratio of the critical molar volume of the solvent to the critical molar volume of the polymeric jumping unit. Consequently, ξ compares the size of the hole required for a solvent molecule to jump with the size of the hole needed for the movement of a jumping unit of the polymer chain.

Upon examination of the three groups, D_{01} , $\gamma \hat{V}_2^* \xi / K_{12}$, and K_{22} , it is easily seen that only D_{01} and $\gamma \hat{V}_2^* \xi / K_{12}$ depend on the nature of the solvent. Furthermore, it has been argued elsewhere³ that

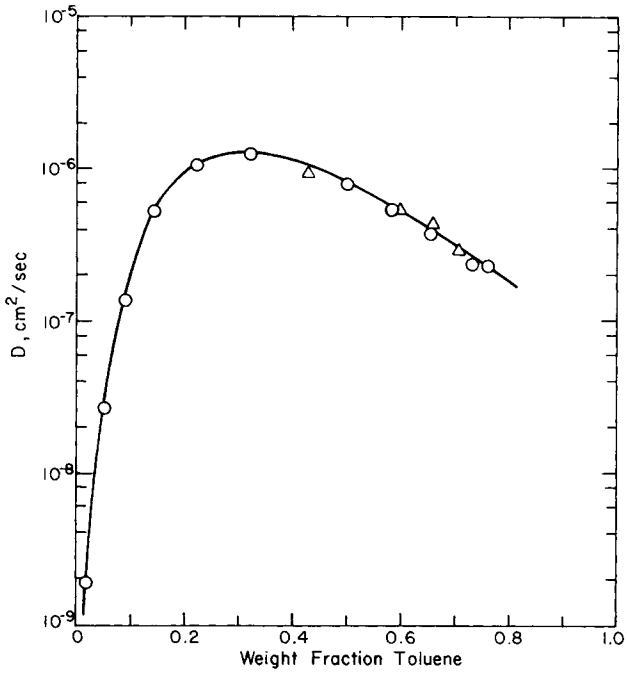


Fig. 2. Diffusivity data for the toluene-polystyrene system at 110°C. Different symbols represent two independent experimental sequences.

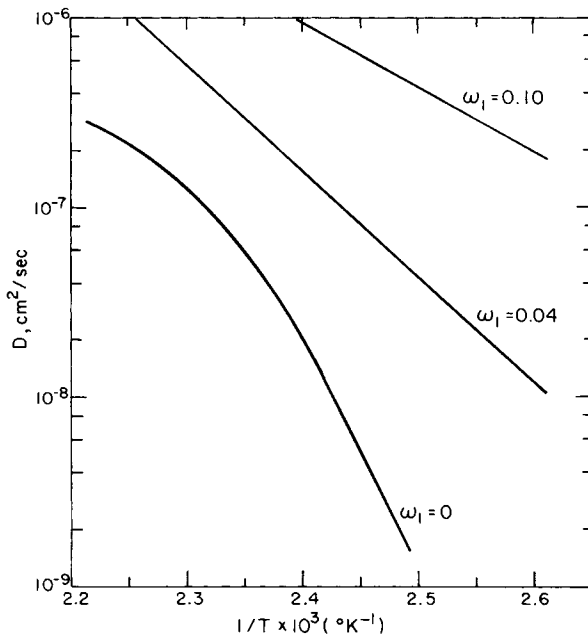


Fig. 3. Temperature dependence of the mutual diffusion coefficient for the toluene-polystyrene system.

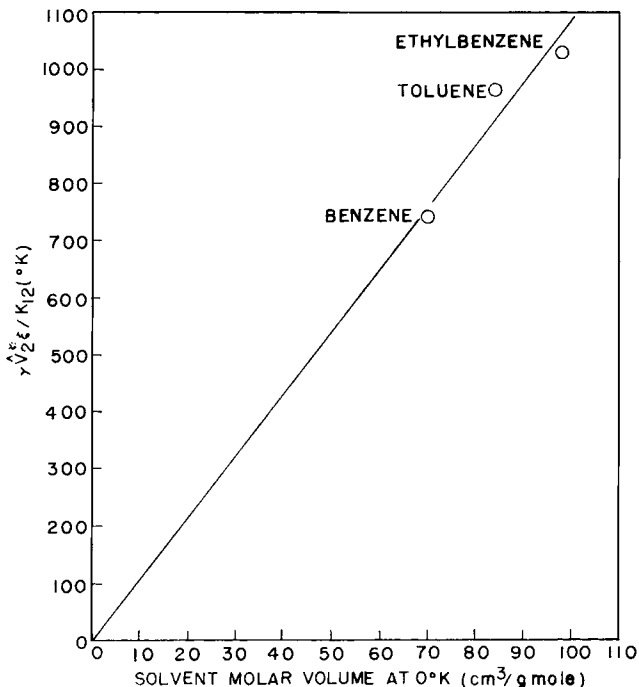


Fig. 4. Dependence of free volume parameter $\gamma \bar{V}_2^* \xi / K_{12}$ on molar volume of the solvent at 0°K for three aromatic hydrocarbons.

it is reasonable to expect that, of these two groups, only $\gamma \bar{V}_2^* \xi / K_{12}$ can be successfully correlated with molecular size. Indeed, it is logical to further deduce that the group $\gamma \bar{V}_2^* \xi / K_{12}$ should be a linear function of the molar volume of the solvent at 0 K. This hypothesis was adequately verified previously³ for a variety of solvents in polystyrene, and it is evident from Figure 4 that it holds particularly well for the series of similar solvents considered here.

The diffusivity data presented here not only describe the diffusion of an important solvent in polystyrene but, in addition, provide a further set of data for the evaluation of theories for diffusion in amorphous polymer-solvent systems. In a previous study,² ethylbenzene-polystyrene diffusivity data were compared with the predictions of the new version of the free volume theory. Although the comparisons were quite encouraging, the concentration dependence of the diffusivity was consistently overestimated by the theory. Though a similar comparison of the toluene diffusion data with theory could be quite illuminating, we prefer to first separate the errors introduced by the thermodynamic theory from those which result from inadequacies in the free volume formulation before attempting such a comparison. Separation of the errors will be attempted in future work using thermodynamic data for the toluene-polystyrene system at elevated temperatures.

This work was supported by the National Science Foundation Grant ENG 74-23095.

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Received August 11, 1977
Revised September 15, 1977