Diffusion of Ethylbenzene in Molten Polystyrene

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Synopsis

Mutual diffusion coefficients are measured for the ethylbenzene–polystyrene system for the temperature range of 115.5°–178°C and for concentrations as high as 70 wt-% ethylbenzene. Experiments were carried out using a quartz spring sorption apparatus which was modified for high-temperature measurements. The diffusivity data are compared with the predictions of a recently developed free-volume theory of polymer–solvent diffusion.

INTRODUCTION

Although molecular diffusion of solvents in molten polymers is important in many polymer processes, relatively few studies have been concerned with the measurement of diffusion coefficients under the conditions of interest in the processing of polymer melts. The experimental problems associated with conducting diffusion studies in molten polymers at elevated temperatures are no doubt partially responsible for the existing deficiency in diffusivity data. Recently, a sorption apparatus was developed[1] for the study of diffusion in polymer solutions at elevated temperatures, and this paper presents the first comprehensive set of data obtained with this apparatus.

In many polymerization processes for the production of polystyrene, sharp gradients in the styrene monomer concentration occur, and the diffusion of the monomer influences the operation of the reactor and the properties of the polymer that is produced. Furthermore, the unreacted monomer must be removed from the polymer melt before an acceptable final product is produced. The role of molecular diffusion in this devolatilization step has become particularly important in recent years as tighter health standards have dictated the removal of potentially toxic volatile impurities from polymers. Consequently, the diffusion behavior of the styrene–polystyrene system is quite important in the design of a process to produce a desirable polystyrene product. The reactivity of the styrene monomer effectively precludes the direct study of this system at elevated temperatures, and therefore the ethylbenzene–polystyrene system was chosen as a model system which should adequately approximate the behavior of styrene–polystyrene solutions.

The principal objective of this study is to determine mutual diffusion coefficients for the ethylbenzene–polystyrene system over ranges of temperature and concentration that are important in commercial processes. Data are presented for the temperature range of 115.5°–178°C and for concentrations as high as 70 wt-% ethylbenzene. To our knowledge, this study is the most comprehensive investigation of the diffusion of a solvent in molten polystyrene. A second objective of this paper is to compare the ethylbenzene–polystyrene diffusivity data

with the predictions of a recently developed free-volume theory of polymer–solvent diffusion.[2,3]

EXPERIMENTAL

The high-temperature sorption apparatus employed in this study is described in detail elsewhere.[1] Basically, the apparatus is a conventional quartz spring sorption balance which was modified for high-temperature measurements. The molten polymer sample is placed in a cylindrical quartz bucket which is suspended from a calibrated helical quartz spring in the main column of the apparatus. The sample chamber is maintained at a fixed temperature by a condensing vapor in an annular space surrounding the diffusion chamber. The penetrant vapor is fed to the sample chamber at a fixed vapor pressure from a reboiler which has an independent temperature controller.

The useful temperature range of the diffusion apparatus is from room temperature to the temperature at which inadequate temperature control in the diffusion chamber is observed. If a suitable heating fluid is utilized, it is possible to obtain good temperature control ($\pm0.03°C$) up to 180°C, but no effort was expended in determining the upper operating temperature limit. The upper limit of the ethylbenzene concentration was set by the pressure limitations of the apparatus. The sorption column and seals were constructed to operate at penetrant vapor pressures no higher than atmospheric, and experiments at 140°C and higher were terminated when the ethylbenzene vapor pressure reached approximately 700 mm of mercury. At the lower temperatures studied here, diffusion data can in principle be obtained over the complete concentration range. However, when the temperature of the solvent feed system approaches the temperature of the polymer sample, small temperature variations can lead to significant variations in the amount of solvent sorbed by the polymer. Consequently, at the lower temperatures, the maximum concentration at which accurate diffusion data can be obtained is set by the characteristics of the temperature controllers used on the apparatus.

In this study, the temperature of the sorption chamber is set by controlling the pressure over the condensing vapor, and the temperature control which is achieved is directly related to the vapor pressure–temperature characteristics of the heat transfer fluid. Dowtherm E was employed as a heat transfer fluid in this study, and it can easily be shown that the temperature control that can be achieved near its boiling point (180.4°C) is significantly better than the control that can be expected for the low-temperature experiments. It was this cruder temperature control which limited the concentration ranges which could be studied at 115.5° and 130°C. In future studies, it is recommended that different heat transfer fluids be used at different temperatures so that a uniformly good control of the sorption chamber temperature can be maintained at all temperature levels.

The transient diffusion experiments were conducted by subjecting the polymer film to a step change in surface concentration. Although this procedure is convenient from an experimental point of view, it is not always a simple matter to deduce meaningful diffusion coefficients from such experiments, mainly because of the strong concentration dependence of the diffusivity for polymer–solvent systems. The difficulty becomes particularly severe when a large con-

centration interval is to be studied using a reasonable number of experiments. Available methods of analyzing step change sorption experiments are reviewed elsewhere,[4] and a new method of analyzing such experiments is proposed. This method is based on the analysis of sorption experiments conducted over a concentration interval small enough so that it can be expected that the diffusivity–concentration relationship can be well represented by an exponential expression, yet large enough so that accurate sorption data can be obtained. For any step change sorption experiment, an average diffusivity can be determined from the initial sorption rate by the standard method of analysis described by Crank.[5] The key to the new method is that this average diffusivity approximates, with less than 5% error, the mutual diffusion coefficient at a known concentration between the initial and final concentrations of the sorption experiment. Hence, each step change sorption experiment yields a single piece of information which directly gives a very good estimate of the mutual diffusion coefficient at a known concentration without relying on additional data from other experiments.

The experimental procedure utilized was a modification of the conventional method of progressing sorption experiments. The total concentration interval was traversed using, in general, only a moderate number of experiments by appropriately varying the sizes of the step concentration changes for the successive experiments. Only the data from experiments with step concentration changes which were considered to be sufficiently small were used to obtain diffusion coefficients. The sorption curves were analyzed using the method described above. In all cases, corrections for swelling of the sample were negligible, and heat effects accompanying the sorption process were estimated to be small.[5] The above experimental procedure made it possible to obtain accurate diffusion coefficients over a large total concentration range using a reasonable number of experiments.

The sorption experiments required from one to six days to effectively reach the equilibrium state consistent with the new vapor pressure level. The time of an experiment can be decreased by reducing the thickness of the polymer sample, but undesirable relaxation effects can occur in thin samples where the rate of molecular diffusion may be comparable to the rate of rearrangement of polymer molecules.[6] The design of experiments to avoid such relaxation effects is considered below.

The diffusivities reported here at 160°, 170°, and 178°C cover the same overall concentration ranges as the diffusion coefficients obtained previously[1] from experiments which were analyzed using a method based on a weighted residual solution[7] of the nonlinear diffusion equation. This procedure is valid for any diffusion coefficient–concentration relationship and takes into account volume change on mixing and phase volume change accompanying sorption. However, the method requires very accurate sorption data since first time derivatives of the sorption curve are utilized in the analysis. Although the diffusivities obtained by the two sets of experiments were in good agreement, it has been found that, in general, a sorption curve is not accurate enough to permit meaningful utilization of the second procedure. The principal difficulty is the inability to collect sorption data with enough accuracy to permit calculation of sufficiently accurate time derivatives of the sorption curve near the end of the step change experiment, where the weight pickup changes very slowly with time. Consequently, all diffusion coefficients reported here were obtained by conducting
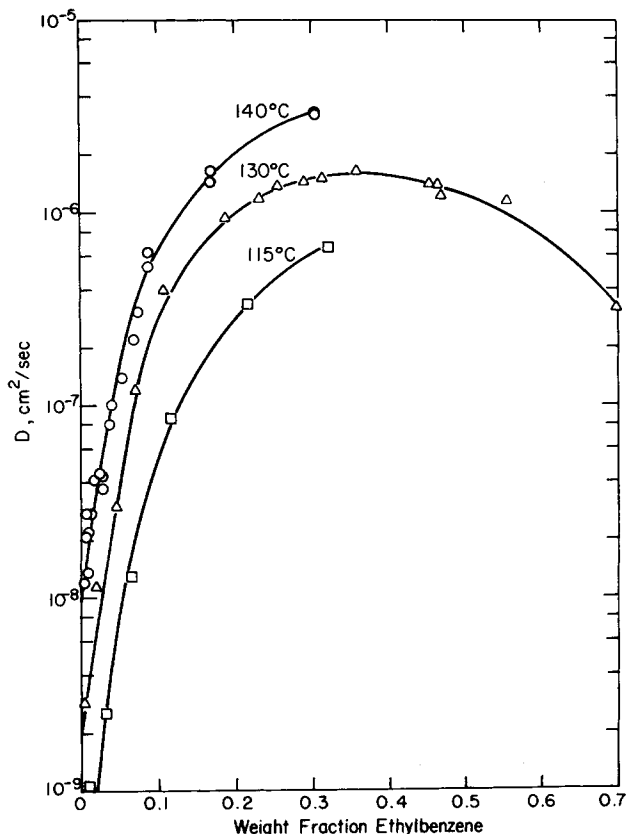
Fig. 1. Diffusivity data for the ethylbenzene–polystyrene system at 115.5°, 130°, and 140°C.

step changes experiments over relatively small concentration intervals. The polymer employed in these measurements was an additive-free commercial polystyrene with a weight-average molecular weight of 275,000.

RESULTS AND DISCUSSION

Diffusivity data for the ethylbenzene–polystyrene system are presented in Figures 1 and 2. Each point on these figures represents the result of a sorption experiment, whereas the lines are simply visual aids for the diffusivity data at each temperature. The data illustrate the strong concentration dependence of the diffusivity; this concentration dependence is more pronounced at lower temperatures and lower solvent concentrations. Such behavior can be regarded as typical for amorphous polymer–solvent systems above the glass transition temperature.[8] Furthermore, it is evident from the data at 130°C that the mutual diffusion coefficient D assumes a maximum value in the middle part of the mass fraction interval. The presence of a maximum in D for polystyrene–solvent systems has been observed previously by Chalyk and Vasenin[9] and by Rehage et al.[10] These investigators also showed that the maximum in the diffusivity–concentration curve shifts to smaller solvent concentrations with increasing temperature. This behavior has also been predicted from the new version of the free-volume theory of diffusion.[3] It is reasonable to infer from the present
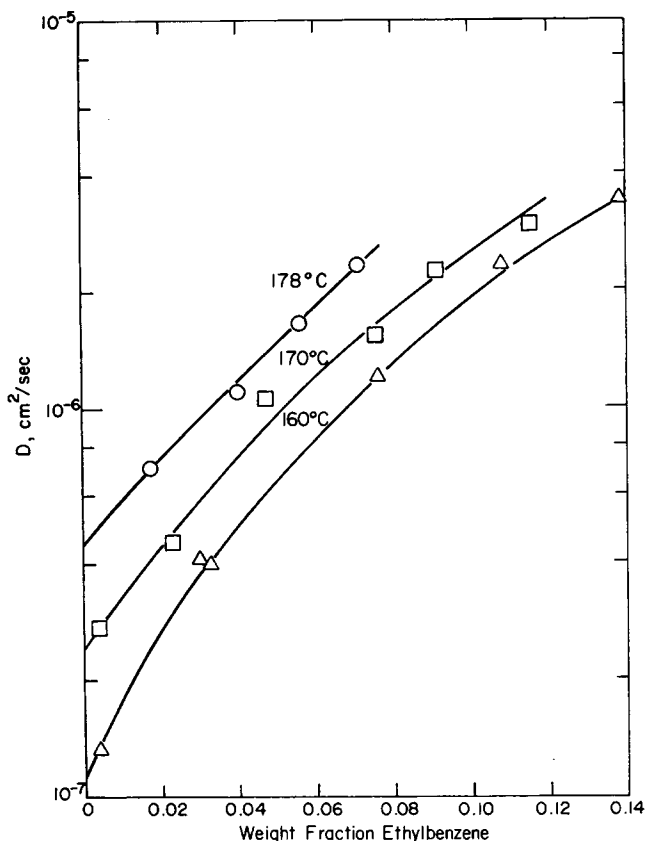
Fig. 2. Diffusivity data for the ethylbenzene–polystyrene system at 160°, 170°, and 178°C.

data at 115.5° and 130°C that the maximum shifts to lower solvent concentrations with increasing temperature, but no definitive conclusions can be drawn from the diffusion data at 140°C.

Anomalous diffusive transport has been observed during sorption experiments with polymers, even at temperatures above the effective glass transition temperature of the polymer–solvent system.[11] For the proper analysis of a sorption experiment, it is necessary to know if such anomalous diffusion behavior can occur at the conditions of the experiment. One method of anticipating conditions under which anomalies can be expected in sorption experiments is by calculation of a dimensionless group called the diffusion Deborah number. It has been proposed[6] that diffusional transport in amorphous polymer–solvent systems can be characterized by this dimensionless group, which is a ratio of the characteristic relaxation time of the polymer–solvent system to the characteristic diffusion time. When the diffusion Deborah number is small (say, less than 0.1), a molecule is diffusing in a purely viscous binary mixture, and conformational changes in the polymer structure appear to take place instantaneously. Diffusive transport is described by the classical theory of diffusion, and conventional sorption experiments can be analyzed using the usual diffusion equation with time-independent boundary conditions. If the diffusion Deborah number is greater than 0.1, rearrangement of polymer molecules is no longer much faster than the diffusion process. Consequently, the influence of relaxation on the
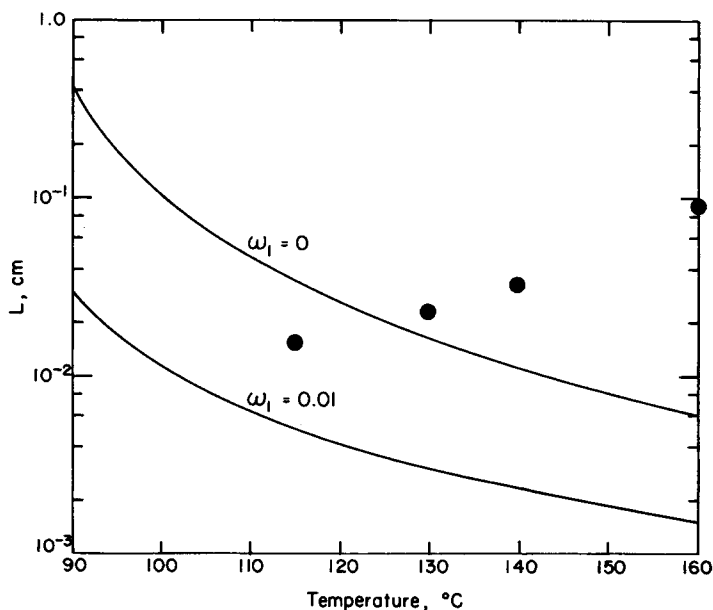
Fig. 3. Temperature and concentration dependence of critical sample thickness for the ethylbenzene–polystyrene system for polymer molecular weight of 275,000. Points are sample thicknesses used in experiments.

diffusion process can, in general, lead to non-Fickian effects in a sorption experiment, and analysis of the experiment is greatly complicated.

Although no general theory has as yet been formulated to describe diffusional transport when relaxation effects are important, the Deborah number concept can be used to determine if an experiment has been conducted under conditions where the polymer relaxation is fast compared to the diffusion process. A procedure has been developed[12] for determining the dependence of the diffusion Deborah number for a sorption experiment on the temperature, polymer molecular weight, sample thickness, and average concentration of the system. This procedure is based on a new version of the free-volume theory of diffusion which is discussed briefly below.[2,3] The result of interest here is the temperature and concentration variation of the minimum sample thickness needed to ensure purely viscous diffusion behavior (diffusion Deborah number less than 0.1) for the ethylbenzene–polystyrene system for a polymer molecular weight of 275,000. This variation of critical sample thickness is depicted in Figure 3. The sample thickness L is for a polymer film exposed to the solvent vapor on one side only. Since the diffusion Deborah number for a particular sorption experiment can be decreased below 0.1 by simply increasing the sample thickness, anomalous effects can be avoided by conducting experiments with sufficiently thick samples. However, it is often necessary to use relatively thin samples so that the experiment can be conducted in a reasonable period of time. Hence, diagrams such as Figure 3 are quite useful in designing experiments from which meaningful diffusion coefficients can be determined.

In Figure 3, the temperature variation of the minimum sample thickness for the ethylbenzene–polystyrene system is shown for two mass fractions, ω_1, of ethylbenzene. Thicker samples must, of course, be utilized as the solvent mass fraction or temperature is lowered. The smallest sample thicknesses used in
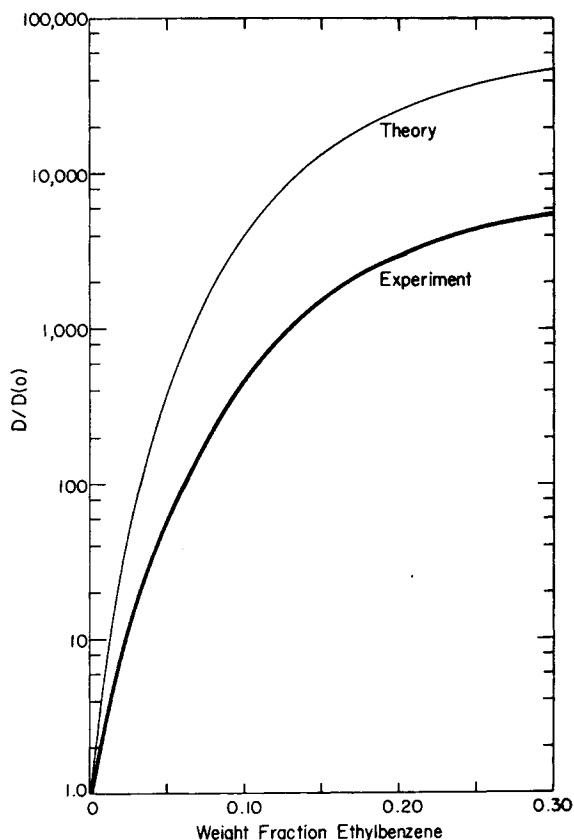
Fig. 4. Comparison of data with theory at 115.5°C.

the ethylbenzene–polystyrene experiments reported in Figures 1 and 2 are shown as points in Figure 3. This figure indicates that all but one of the experiments of this study were conducted under conditions where classical diffusion theory should be applicable. The first data point at 115.5°C is questionable, but the remainder of the experiments should yield meaningful diffusion coefficients.

A new version of the free-volume theory of diffusion has been recently developed[2,3] for the prediction of the concentration, temperature, and molecular weight dependence of diffusion coefficients in amorphous polymer–solvent systems. This theory is based on the free-volume theory of molecular transport, the thermodynamic theory of Flory,[13] and the entanglement results of Bueche.[14] The parameters of the theory are determined from a limited amount of experimental data, taken primarily on essentially pure liquids. For example, the free volume parameters of the theory can be determined from viscosity data for the pure solvent and pure polymer and mutual diffusion data for a system consisting of a trace of solvent in the polymer. In this study, the diffusivity data at 160°, 170°, and 178°C were extrapolated to zero solvent concentration to produce values of $D(0)$ for utilization in the procedure for the determination of the parameters of the free-volume theory.

Comparisons of the theoretical predictions for the ethylbenzene–polystyrene system with the experimental data for the six temperatures considered are presented in Figures 4–8. In the preparation of these figures, the experimental
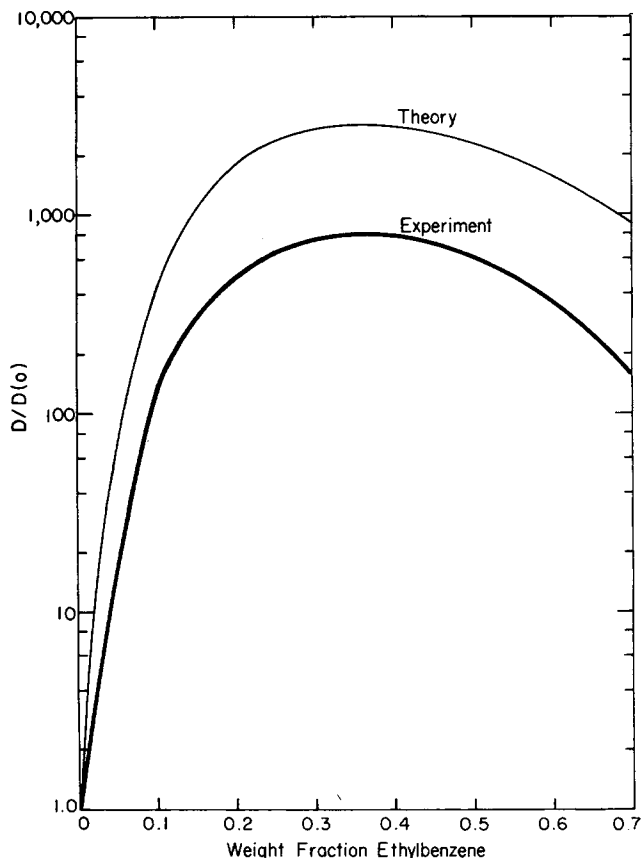
Fig. 5. Comparison of data with theory at 130°C.

values of the diffusion coefficients at zero solvent concentration, $D(0)$, were obtained from careful extrapolations of the data for all temperatures except 115.5°C. At this temperature, it was not possible to extrapolate the data with any reasonable degree of confidence, and the value of $D(0)$ was calculated from the theory. Finally, we note that there are minor differences between the present theoretical results and the theoretical results presented earlier.[3] These differences are due to the utilization of a more sophisticated extrapolation procedure for the determination of the $D(0)$ values used in the evaluation of the free-volume parameters.

From Figures 4–8, it is evident that the shapes of the theoretical and experimental curves are quite similar, but the theory consistently overestimates the concentration dependence of the diffusivity. On the other hand, there is excellent agreement between theory and experiment for the concentration at which the maximum in the diffusivity curve occurs at 130°C. We believe that these results are quite encouraging since these predictions cover a range of concentration where the diffusion coefficient changes by nearly four orders of magnitude, and the only mass transfer information used in the theory is the limited diffusivity data at infinite solvent dilution. Furthermore, we know of no other theory that can even qualitatively predict the behavior which is experimentally observed for polymer–solvent systems over large concentration ranges. It should also be noted that the prediction of mutual diffusion coefficients is particularly
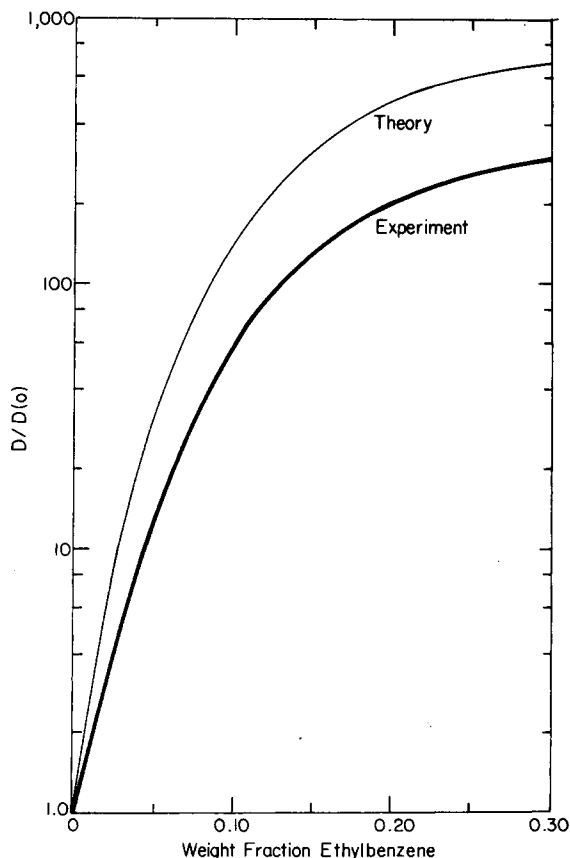
Fig. 6. Comparison of data with theory at 140°C.

difficult because it is necessary to utilize a theory of molecular transport in liquids in conjunction with a thermodynamic theory for the liquid state. Finally, we note that errors in the derived parameters of the theory are magnified because of the nearly exponential character of the concentration dependence of D.

From the comparisons of data and theory presented here, it seems appropriate to conclude that the proposed theory provides an adequate estimate of the concentration dependence of the diffusivity in amorphous polymer–solvent systems. Further effort will be expended in attempting to determine the reason for the discrepancy between theory and experiment. In particular, the errors introduced by the Flory theory will be separated from those resulting from inadequacies in the free-volume theory by utilizing thermodynamic data obtained at elevated temperatures.

A discussion of the theory utilized above is not included here since this would be lengthy and is presented in detail elsewhere.[2,3] However, it is useful to summarize the basis of the theoretical treatment to judge more clearly what is involved in the comparison of theory and experiment. The theory is based on the determination of the mutual diffusion coefficient from the self-diffusion coefficients of the solvent and polymer and from the chemical potential of the solvent. The chemical potential of the solvent and the specific volume of the binary mixture are determined using the thermodynamic theory of Flory.[13] This involves using extensive pure-component data and a limited amount of mixture
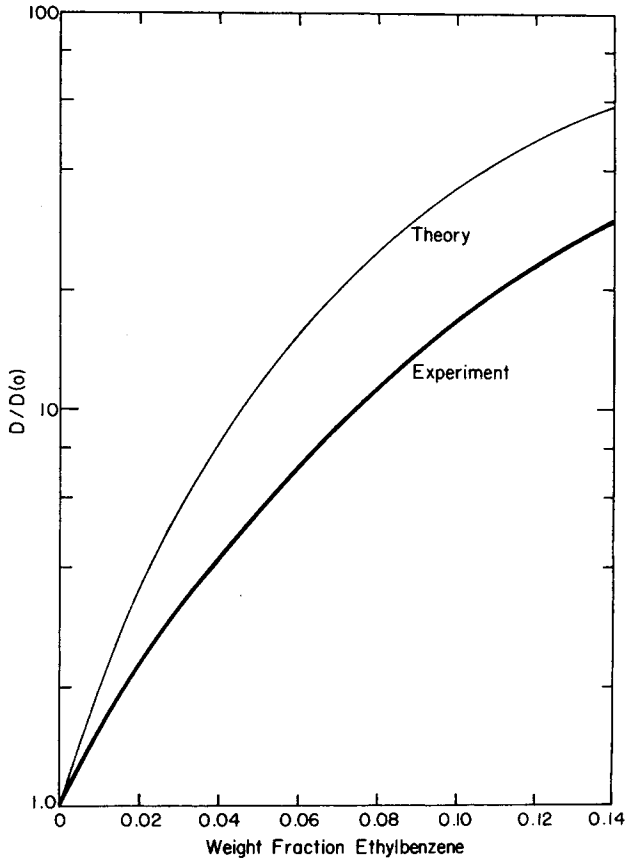
Fig. 7. Comparison of data with theory at 160°C.

data. The self-diffusion coefficients are determined using a new version of the free-volume theory of transport. As noted above, the free-volume parameters can be determined from viscosity data for the solvent and polymer and from a limited amount of mutual diffusion data taken in the limit of zero solvent concentration. In addition, the entanglement theory of Bueche[14] must be utilized in the determination of the polymer self-diffusion coefficient. Adequate estimates of the parameters in this theory are available. It is evident that the experimental data needed for the evaluation of the parameters of the theory are taken primarily on pure liquids. Hence, the theory is truly predictive in the sense that a property of a binary system is determined over wide ranges of temperature, composition, and molecular weight, and this is done using a very limited amount of mixture data in conjunction with data taken on the pure components. The theory thus follows the classical approach of attempting to predict mixture properties primarily from properties of the pure components.
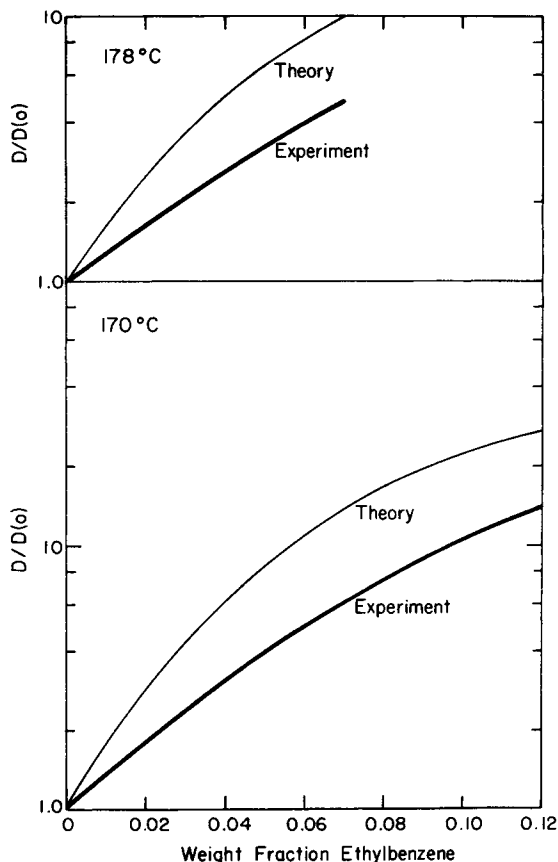
Fig. 8. Comparison of data with theory at 170° and 178°C.

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