

Diffusion in Concentrated Polystyrene Solutions

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Synopsis

The wedge interferometer technique was used to measure the diffusion coefficients for concentrated solutions of polystyrene. A wide range of molecular weights, all monodisperse except for one, and 14 solvents were studied. Reproducibility of the data was demonstrated in the concentrated region, and good agreement with the sparse literature was observed. The experimental results are discussed and analyzed in terms of current knowledge and theories. In the concentrated region, the solvent type plays a significant role in determining the diffusion coefficient. Its effect cannot be explained simply in terms of hydrodynamics nor the molecular structure of the solvent. In cyclohexanone the diffusion coefficient was found to increase with polymer molecular weight up to 100,000 and to become independent thereafter.

INTRODUCTION

Molecular diffusion in binary systems of large polymer molecules and small solvent molecules takes on special characteristics and demonstrates markedly different behavior as the relative proportions of the two species are varied over the complete spectrum. The two extremes of this spectrum, dilute polymer solutions and essentially bulk polymers, form special cases which have been isolated for study. Specific reasons for interest in either extreme have been identified, experimental techniques to effect their study have been developed, and more or less adequate theories to aid their understanding have been advanced. These developments are documented briefly in two sections that follow.

On the other hand, relatively little is known about the middle region between the above mentioned extremes which we will refer to as concentrated polymer solutions. At this point we will not attempt to define the concentration limits of this region. This region is of considerable importance since numerous polymer processing and forming operations that involve mass transfer occur here. In addition, diffusion in this region may be of great importance in polymerization.^{1,2} Therefore, the lack of scientific development in this region is not owing to a lack of interest. Experimental studies have not been numerous because the better techniques work best for either low viscosity liquids or solids but not extremely

viscous fluids. Theories have not been forthcoming because of the complexity of the problem.

In the past few years, some interest has centered around the use of a simple wedge interferometer³⁻¹³ which offers in principle an attractive method of measuring diffusion coefficients for concentrated polymer solutions. It seems ideally suited for this purpose since the diffusion field is small, and thus the time required for an experiment can be kept short. It can handle very viscous fluids although there is a practical upper limit for convenient manipulation. Further, methods of data analysis exist which permit the calculation of the diffusion coefficient from one experiment for all polymer concentrations represented.¹⁴ While numerous investigations employing this technique have been reported, only a minimal number of systems have been studied and very little attention has been paid to the accuracy or reproducibility of the results. Therefore, the utility of the technique is unproved, and not much progress has been made toward understanding diffusion in concentrated solutions.

It is the purpose of this paper to report a considerable amount of data obtained by the wedge interferometer technique which allows some insight into its utility and limitations. Specifically, the questions of reproducibility and comparison with other investigations are considered. In addition, an examination of relevant questions about diffusion in concentrated solutions has been made. However, neither line of inquiry may be considered complete, especially the latter. The systems employed here were polystyrene over a wide range of molecular weight and numerous solvents.

Before going on to the results of this investigation, we will examine various aspects of diffusion in the extreme regions of the concentration spectrum, as this will aid our discussion of the concentrated region.

DIFFUSION IN DILUTE POLYMER SOLUTIONS

Of the two extremes, the dilute region has been studied most thoroughly and is better understood. Interest in this region has arisen primarily from the need to know more about the structure and molecular weight of polymer molecules. Much of the experimental work has involved observing the boundary spreading which occurs in the ultracentrifuge;¹⁵⁻¹⁹ however, several investigations have used static-type diffusion cells commonly employed in liquid diffusion.²⁰⁻²⁴

Theories for infinite dilution have been developed from the principles of hydrodynamics. Conceptually, these theories consider the diffusive motion of the isolated polymer molecule through the solvent and quantitatively attempt to obtain the frictional coefficient f_0 in the Einstein equation

$$D_0 = kT/f_0 \quad (1)$$

for this motion.²⁵ Of most pertinence for our purposes is the result for flexible polymer chains given by Kirkwood and Riseman,²⁶ which is

$$f_0 = \frac{6\pi\eta_0 \left(\frac{3\sqrt{\pi}}{8}\right) R_G}{1 + \frac{6\pi\eta_0 \left(\frac{3\sqrt{\pi}}{8}\right) R_G}{Z\zeta}} \quad (2)$$

The terms in this equation are the solvent viscosity η_0 , the monomeric friction coefficient ζ , the number of chain atoms in the molecule Z , and the radius of gyration of the coiled polymer molecule R_G . The monomeric friction coefficient describes the hydrodynamic resistance of an individual chain atom or group moving through the solvent. It is generally believed that this resistance is so large that little solvent flows through the coil so that eq. (1) reduces to a form analogous to Stokes' law

$$f_0 = 6\pi\eta_0 \left(\frac{3\sqrt{\pi}}{8}\right) R_G \quad (3)$$

if $(3\sqrt{\pi}/8)R_G$ is considered the equivalent hydrodynamic radius for the almost impenetrable polymer coil. The radius of gyration is related to the root mean square end-to-end distances, $\langle r^2 \rangle^{1/2}$, and the effective bond length, b , by

$$R_G = \frac{\langle r^2 \rangle^{1/2}}{\sqrt{6}} = \frac{b\sqrt{Z}}{\sqrt{6}} \quad (4)$$

The theory predicts that D_0 should be inversely proportional to $M^{0.5}$ if b is constant, as it would be in a theta solvent. If the solvent interacted strongly with the polymer, b may depend on M to a small power of, say, 0.05 to 0.10. This would make D_0 inversely proportional to M to the 0.55 to 0.60 power, as shown by a number of dilute solution studies.¹⁵⁻²⁴

As the polymer concentration increases slightly from the limit of infinite dilution, the diffusion coefficient may be expected to vary, as has been shown experimentally. This initial concentration dependence has been explored in the literature.²⁰⁻²² It is well recognized that eq. (1) should be written as

$$D = \frac{kT}{f} \left(\frac{\partial \ln a_2}{\partial \ln \rho_2} \right) \quad (5)$$

when applied to nonideal solutions not in the limit of infinite dilution.^{2,25-27} The term in parentheses provides the connection between the definition of D in terms of a concentration gradient and the mechanical definition of the friction coefficient f in terms of real forces. For dilute enough polymer solutions, this thermodynamic factor can be written in terms of the virial expansion of the activity. The friction coefficient f can be measured

independently by the ultracentrifuge and has been found to increase as the polymer concentration, ρ_2 , increases.²⁵ Over a limited range, this change is linear, so it is written

$$f = f_0(1 + k_s\rho_2 + \dots). \quad (6)$$

Insertion of the thermodynamic expansion and eq. (6) into eq. (5) gives

$$D = D_0[1 + (2MA_2 - k_s)\rho_2 + \dots] \quad (7)$$

where A_2 is the thermodynamic second virial coefficient. Equation (7) provides the basis for understanding the limiting concentration dependence of D in terms of two solution properties (one thermodynamic, A_2 , and the other hydrodynamic, k_s). The second virial coefficient²⁵ for polymer solutions is normally in the range of 10^{-4} to 10^{-3} mole-cc/g² and is inversely proportional to M raised to a power of 0.05 to 0.25. At the theta temperature, A_2 is zero, and as the temperature is lowered beyond this point, A_2 becomes negative but the polymer soon precipitates from solution. In general, however, it can be concluded that $2A_2M$ is positive and proportional to $M^{0.75-0.95}$.

The hydrodynamic coefficient k_s has not been investigated as thoroughly as A_2 . However, Pyun and Fixman²⁸ have developed a theory near the theta condition which predicts that k_s is proportional to $M^{1/2}$. Kotaka and Donkai²⁹ recently gave an experimental verification of this for the system polystyrene-cyclohexane at 35°C. As the thermodynamic quality of the solvent is improved, it may be that k_s depends on a higher power of M since it has been suggested that it is proportional to the intrinsic viscosity $[\eta]$.²

From the above, it is clear that the concentration dependence of D in the dilute region strongly depends on the molecular weight of the polymer, M . We can expect that $dD/d\rho_2$ will be negative at low M , positive at high M , and essentially zero at some intermediate molecular weight. The exact dependence will depend on the thermodynamic interactions with the solvent. The effect of M on the concentration dependence is such as to make D less dependent on M as the concentration is increased. Of course, eq. (7) is applicable only to quite dilute solutions, but it seems plausible that the sign of $dD/d\rho_2$ given by this term will be maintained from $\rho_2 = 0$ into the concentrated region.

DIFFUSION IN BULK POLYMERS

The other extreme consists of diffusion of solvent molecules in essentially solid polymer. Interest in this region stems from concerns about the barrier properties of the polymer, certain membrane separation processes, and devolatilization, to mention a few. Experimental techniques include sorption kinetics or permeation with the solvent in the form of a liquid or a vapor. The nature of the behavior depends very much on whether the polymer is above or below its T_g . The behavior below T_g may be

very complex;³⁰ however, for our purposes here, we need only consider the more well-defined behavior that prevails above T_g .

No truly quantitative theories have emerged, but the experimental work has led to a consistent and conceptually well-defined picture. In the limit of zero solvent content, this picture envisions individual solvent molecules moving through the polymer by an activated diffusion process which requires cooperative segmental motion of the polymer without requiring any net motion of the entire polymer molecule. It is believed that the diffusion coefficient is independent of the polymer molecular weight³¹ so long as it is high enough not to affect the free volume. Even light crosslinking probably does not affect D . The activation energy for diffusion is usually quite large (~ 40 kcal/mole) and seems to depend more on the polymer than the penetrant, in contrast to smaller gas molecules where the activation energy is definitely dependent on molecular size.³² The absolute magnitude of the diffusion coefficient is very dependent on the molecular size and structure of the penetrant,³¹ with values lower than 10^{-13} cm²/sec in some cases. Hydrodynamics of the solvent is definitely not a factor at this extreme.

As the content of the solvent increases, D increases very rapidly apparently owing to the plasticizing effect which permits freer motion of the polymer segments. The thermodynamic interactions of the polymer and the solvent is most likely a factor here. Free volume theories have been rather successful in correlating this concentration dependence,³¹ however.

EXPERIMENTAL

The wedge interferometer, ancillary equipment, and experimental procedure were essentially the same as reported earlier.¹¹ This technique involves bringing a more concentrated polymer solution (weight fraction ω_{20}) into contact with a less concentrated solution (weight fraction $\omega_{2\infty}$) in an optical wedge where free diffusion occurs. Most work in the literature employs pure solvent for the latter, i.e. $\omega_{2\infty} = 0$; however, for reasons cited later, we have found it advantageous to use solutions containing as much as 10% polymer.

A series of polystyrene polymers covering a wide range of molecular weights were used. As seen in Table I, eight were essentially monodisperse, but one, Styron 690, was quite polydisperse. A total of 14 solvents (see Table II) were used, but approximately one half of the experiments were with cyclohexanone. The selection of solvents was made within the requirements of low volatility and insurance of an adequate refractive index difference.¹¹

The upper polymer concentration, ω_{20} , for a given experiment was selected to keep the solution viscosity from being too high or low to permit manipulation within the wedge. By necessity, ω_{20} varied with molecular weight of the polymer, as may be seen in Table III.

TABLE I
 Polystyrene Samples^a

Polymer	\bar{M}_w/\bar{M}_n
Peak MW ^b	
4,800	1.087
19,750	1.062
50,000	1.041
97,200	1.021
402,000	1.048
830,000	1.121
860,000	<1.15
S109	
$\bar{M}_w = 187,000$	1.06
$\bar{M}_n = 176,000$	
Styron 690	
$\bar{M}_w = 358,000$	2.38
$\bar{M}_n = 150,000$	

^a All of these polymers were provided by the Dow Chemical Company through the courtesy of J. G. Hendrickson, J. L. Duda, and others.

^b Peak molecular weight is defined by the position of the maximum on a gel permeation curve.

 TABLE II
 Diffusion Data for S109 in Various Solvents

Solvent	η_0 ^a	ω_{20}	$\omega_{2\infty}$	$D \times 10^7$, cm ² /sec
Methyl ethyl ketone	0.40	0.40	0.20	10.4
Methyl isobutyl ketone	0.55	0.30	0.10	3.10
Methyl isobutyl ketone	0.55	0.30	0.10	3.25
Toluene	0.55	0.30	0.10	15.4
Toluene	0.55	0.30	0	16.6
Ethylbenzene	0.63	0.30	0.10	13.7
<i>n</i> -Butyl acetate	0.69	0.30	0.10	6.40
<i>n</i> -Butyl acetate	0.69	0.30	0.10	5.62
Acetyl acetone	0.71	0.30	0.10	3.00
Chlorobenzene	0.76	0.30	0.10	12.8
<i>o</i> -Xylene	0.77	0.30	0.10	8.36
Amyl acetate (primary)	0.77	0.30	0.10	6.40
Ethyl glycol acetate	1.10	0.30	0.15	5.00
1,4-Dioxane	1.20	0.30	0.10	6.10
1,2,4-Trichlorobenzene	1.33	0.25	0	8.45
Cyclohexanone	2.00	0.30	0.15	5.20
Cyclohexanone	2.00	0.30	0.10	4.22
Cyclohexanone	2.00	0.20	0	4.94
Cyclohexanone	2.00	0.25	0	5.00
Cyclohexanone	2.00	0.30	0	5.05
Dimethyl adipate	2.69	0.25	0.10	0.76

^a Solvent viscosity at 25°C.

TABLE III
Diffusion Data for Various Polymer Molecular Weights

Polymer MW	Solvent	ω_{20}	$\omega_{2\infty}$	$D \times 10^7$, cm ² /sec
4,800	cyclohexanone	0.60	0	0.75
19,750	cyclohexanone	0.542	0	2.13
19,750	cyclohexanone	0.40	0	1.97
19,750	cyclohexanone	0.50	0.30	2.35
50,000	cyclohexanone	0.40	0	3.84
50,000	cyclohexanone	0.40	0.20	3.84
97,200	cyclohexanone	0.25	0	5.15
97,200	cyclohexanone	0.30	0	4.46
97,200	cyclohexanone	0.35	0	4.70
97,200	chclohexanone	0.35	0	4.22
97,200	chclohexanone	0.35	0.15	4.38
97,200	toluene	0.35	0	13.8
97,200	1,2,4-trichlorobenzene	0.35	0	5.63
Styron 690	cyclohexanone	0.30	0	4.22
Styron 690	cyclohexanone	0.25	0.10	3.80
402,000	cyclohexanone	0.30	0	4.22
402,000	<i>n</i> -butyl acetate	0.20	0	5.00
402,000	1,4-dioxane	0.198	0	4.80
830,000	cyclohexanone	0.20	0	4.55
860,000	cyclohexanone	0.10	0	4.37

For all solvents, the refractive index of the polymer solutions was linear in the mass concentration of the solution ($\rho_2 =$ mass of polymer/volume of solution as calculated by pure component densities) over the range of concentrations employed. All data analyses were performed using concentrations in terms of ρ_2 rather than ω_2 .

No attempt was made to thermostat the interferometer except to hold room temperature constant at about 25°C. Slight heating within the wedge resulted from the light source; however, this effect is not very significant.

Numerous photographs were taken of the fringe patterns during the course of a given experiment. These results were analyzed in the fashion indicated next.

CALCULATION OF DIFFUSION COEFFICIENTS

If it is assumed that there is no volume change on mixing for these systems, then the following simple equation can be used for data analysis:¹⁴

$$D = -2 \frac{d\eta}{d\rho^*} \int_1^{\rho^*} \eta d\rho^* \quad (8)$$

where $\eta = x/2t^{1/2}$ and $\rho^* = (\rho_1 - \rho_{2\infty})/(\rho_{20} - \rho_{2\infty})$. Any errors owing to neglect of volume changes on mixing are less than the reproducibility of the results.

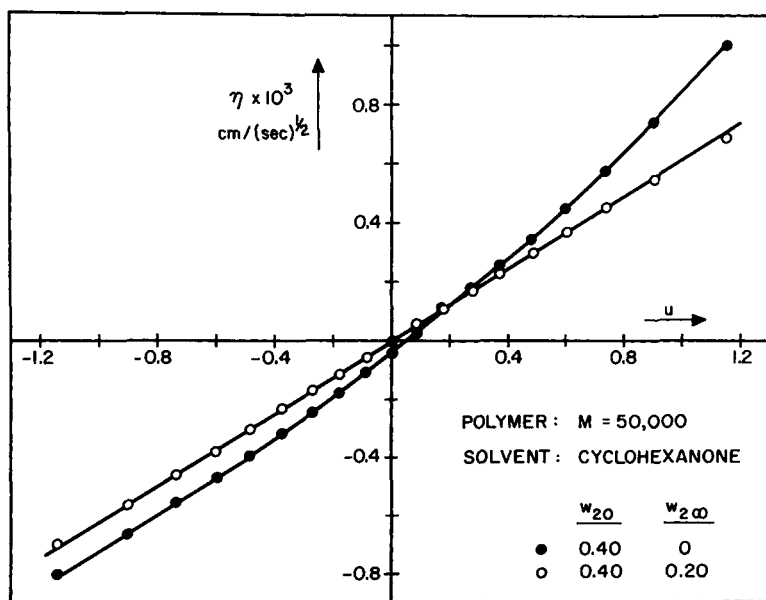


Fig. 1. Transformed concentration profiles. Curved line employed pure solvent ($w_{2\infty} = 0$), while straight line did not.

The procedure consisted of converting the photographic data into plots of ρ^* versus x .¹¹ Plots of x versus $t^{1/2}$ were used to develop a master curve of ρ^* versus η . Each ρ^* was transformed into the variable u defined by

$$\rho^* = \frac{1}{2} [1 - \text{erf}(u)]. \quad (9)$$

From this, plots of η versus u were made, examples of which are shown in Figures 1 and 2. It can easily be shown that when these plots are linear and pass through the origin, D is independent of concentration and equal to $(d\eta/du)^2$. Curvature on such a plot indicates a concentration dependence of D and thus requires more elaborate calculation procedures.

Data from various experiments reported here ($w_{2\infty} = 0$ in each case) were subjected to an analysis to yield D as a function of ρ_2 . Use was made of the observation that the extremes of plots of η versus u often become linear asymptotically.¹¹ These regions are characterized by the slopes $(d\eta/du)_{\rho^* \rightarrow 0}$ and $(d\eta/du)_{\rho^* \rightarrow 1}$ and the intercepts k_0 and k_1 their extrapolations make on the $\eta = 0$ axis.

The integral $\int_1^{\rho^*} \eta d\rho^*$ in eq. (8) was calculated by a combination of graphic and analytical integrations. The first increment of the integral was calculated by the formula

$$\int_1^{\rho^*} \eta d\rho^* = \left(\frac{d\eta}{du} \right)_{\rho^* \rightarrow 1} \left[\frac{e^{-u^2}}{2\sqrt{\pi}} + k_1(1 - \rho^*) \right] \quad (10)$$

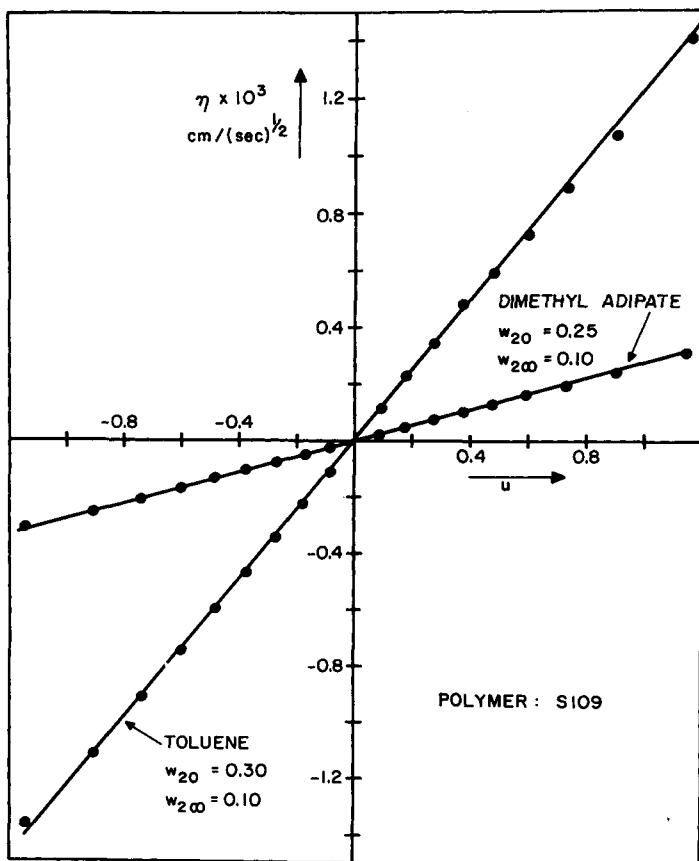


Fig. 2. Transformed concentration profiles showing large effect of solvent used.

which is valid within the linear region near $\rho^* = 1$. This avoids difficulties with graphic integration in this limiting region. After starting the integration in this way, the integral was calculated for all other ρ^* values graphically from a plot of ρ^* versus η . The slope $d\eta/d\rho^*$ in eq. (8) was determined by evaluating $d\eta/du$ graphically from plots such as shown in Figure 1 and then using

$$\frac{d\eta}{d\rho^*} = -\sqrt{\pi} e^{u^2} \left(\frac{d\eta}{du} \right). \quad (11)$$

These results were inserted into eq. (8) to get D at each ρ^* . The limiting values of D at $\rho^* = 0$ and 1 were computed from

$$D_0 = \left(\frac{d\eta}{du} \right)_{\rho^* \rightarrow 0}^2 \quad (12)$$

$$D_1 = \left(\frac{d\eta}{du} \right)_{\rho^* \rightarrow 1}^2. \quad (13)$$

Figure 3 shows the results of calculations by the above procedure for three polymers. Various features of these results are in good accord with the theories for dilute solution discussed earlier. First, D_0 decreases with M and does so at a rate in rather quantitative agreement with the theory. Second, the concentration dependence is in agreement with what may be expected from theory in that $dD/d\rho_2$ is negative at low M , positive at high M , and zero at an intermediate value. However, it is noted that the

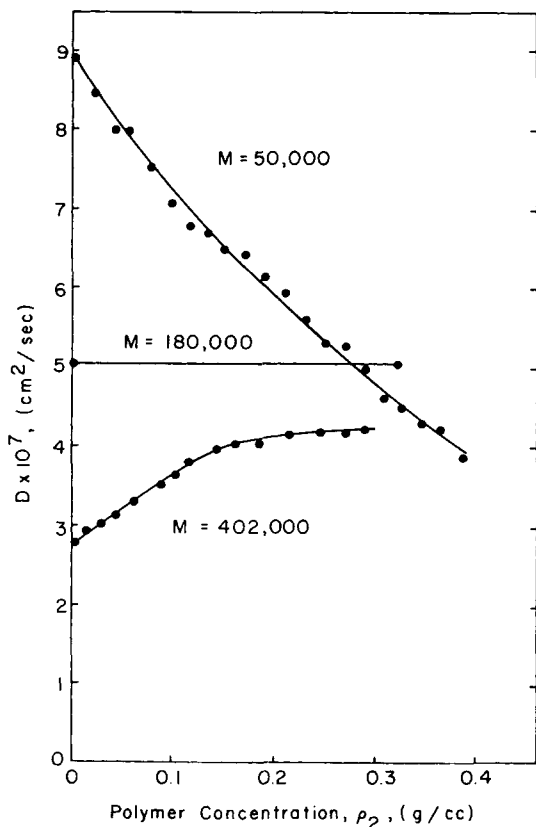


Fig. 3. Diffusion coefficients calculated by eq. (8). Solvent cyclohexanone.

absolute magnitude of D_0 varies considerably from the prediction of the Kirkwood-Riseman theory. Duplicate experiments showed that the detailed features of these diagrams were not very reproducible, although the sign of the concentration dependence and the value of D in the concentrated regions were generally well preserved from experiment to experiment.

The difficulty here resides in several factors. First of all, extraction of values of D which vary as strongly as shown in Figure 3 for $M = 50,000$

from the results of experiments such as these is probably beyond the practical information content of the data, although in principle it should be there. Second, the analysis implicitly assumes that no mixing or flow occurs within the wedge. This is not likely to occur with very viscous solutions, but it may occur with low-viscosity solvents.¹³ The latter difficulty can be readily solved by using instead of pure solvent a polymer solution of concentration $\omega_{2\infty}$, where $\omega_{2\infty} < \omega_{20}$. Such a solution should be low enough in viscosity to enter the wedge readily from the side but viscous enough to avoid mixing and flow induced by surface tension. The difference in refractive indices of the two solutions should be sufficiently large to yield adequate fringe deflection. The first problem noted above can be partially remedied in this way also, since a general feature of Figure 3 and many others like it is that the concentration dependence of D seems to lessen considerably above about 10% polymer.

Figure 1 illustrates dramatically the beneficial effect that results from the above suggestion. The experiment for a 40% solution versus pure solvent, $\omega_{2\infty} = 0$, shows considerable curvature whose analysis via eqs. (8) to (13) yields the D versus ρ_2 shown in Figure 3. On the other hand, the data generated by diffusion between a 40% and 20% solution show that in this region D is effectively constant. There is undoubtedly a considerable concentration dependence of D between 0 and 20% polymer, but we cannot determine it adequately for the reasons pointed out earlier. Further, this difficulty prevents us from accurately obtaining D from 20% to 40% polymer in such an experiment. Figure 3 shows considerable concentration dependence in this region, even though the comparison experiment with $\omega_{2\infty} = 0.20$ shows D to be essentially constant here. It should be noted that the pure solvent experiment gives a D in the limit of $\rho^* = 1$ in perfect agreement with the other experiment. That this will be so can be seen by noting that in Figure 1 the two curves become parallel in this limit, although one is vertically displaced from the other.

This observation has prompted us to speculate that D values calculated by eq. (13) for our experiments with pure solvents are valid and meaningful for $\omega_2 = \omega_{20}$ and an undefined range that may extend considerably below this even when values calculated by eqs. (8) to (13) are in considerable error for the reasons given above. The fundamental justification for this speculation is as follows. In the limit of $\rho^* = 1$, the D calculated depends only on the slope (i.e., the relative alignment of the data points) of the η -versus- u plot; however, away from this limit it depends also on the absolute vertical alignment of these points which may be influenced by events on the dilute solution side. In a free diffusion field, the distance between any two points of fixed concentration is proportional to the square root of time. Therefore, if, owing to some difficulty in the dilute region, the origin of the diffusion field is improperly located by calculation,^{11,14} then every η calculated in the concentrated region (where this difficulty does not exist) will be in error by a constant additive amount. An experiment justification for this proposal is given in Tables II and III.

EXPERIMENTAL RESULTS

Tables II and III tabulate the experimental results along with the ω_{20} and $\omega_{2\infty}$ values so that the conditions of each experiment can be seen readily. In experiments where $\omega_{2\infty} \neq 0$, the diffusion coefficient has been judged to be substantially constant at the value given for the range of concentrations represented. In a few cases, some concentration dependence was detected at low concentrations, but this has been ignored. In experiments where $\omega_{2\infty} = 0$, the diffusion coefficient given was calculated via eq. (13) and is judged to be applicable from $\omega_2 = 0.1$ or 0.2 up to ω_{20} . These tables permit a number of checks on reproducibility within fixed values of ω_{20} and $\omega_{2\infty}$ and comparisons between cases where these limits have been varied. For the D values tabulated, there seems to be no trend, as ω_{20} or $\omega_{2\infty}$ are varied. Any differences noted seem to be within the limits of reproducibility for a fixed set of ω_{20} and $\omega_{2\infty}$ thus justifying the use of these values. In view of this, there are eight sets of data (same polymer and solvent) in Tables II and III containing from two to five data points available for ascertaining reproducibility. The average absolute deviation from the mean within a set ranged from 0% to 6.5%, with the average over all eight sets being 4.4%. It therefore seems fair to state that these results are reproducible within $\pm 5\%$ about the mean. A comparison of these data with others from the literature will be made later.

DISCUSSION

The experiments reported here were designed primarily to allow an examination of the effect of the solvent and the polymer molecular weight on the diffusion coefficient in the concentrated region. The data are arranged in Tables II and III according to these two planned sequences. These data will be discussed and interpreted along these lines; however, before doing so we will discuss two other important points.

First, we call attention to the lack of concentration dependence of D in the concentrated region as contrasted to the dilute and bulk extremes. Roughly one half of the data in Tables II and III were taken with $\omega_{2\infty} \neq 0$, and most show substantially no concentration dependence of D in the general range of $\omega_2 = 0.1$ to 0.5 . This is not to say that D is absolutely constant, but merely that any variations are small. Because of this, we feel that values in Tables II and III can be compared with one another even though the concentration limits of the experiments are sometimes different. There are several reports in the literature using a similar experimental approach which indicate a relatively concentration independent plateau corresponding roughly to the concentration region indicated here.^{5,8} Recent results³³ with diffusion of solvents through highly swollen, crosslinked polymer membranes provide further evidence that D is substantially constant in this region.

TABLE IV
Comparison with Other Polystyrene Diffusion Data

Investigator	$T, ^\circ\text{C}$	Literature data			This work ^a	
		MW	Solvent	$D \times 10^7, \text{cm}^2/\text{sec}$	$D \times 10^7, \text{cm}^2/\text{sec}$	$D \times 10^7, \text{cm}^2/\text{sec}$
Rahge and Ernst ⁵	30	180,000	ethylbenzene	14.5 ^b	13.7	13.7
Rahge and Ernst ⁵	30	180,000	toluene	17	15.4, 16.6	15.4, 16.6
Ueberreiter ³⁴	20	153,000	toluene	16.8, 15.6 ^c	15.4, 16.6	15.4, 16.6
Ueberreiter ³⁴	20	32,000	amyl acetate	4.3, 3.53	6.40 ^d	6.40 ^d
Chalykh and Vasenin ⁸	20	120,000	butyl acetate	5.3 ^b	6.40, 5.62	6.40, 5.62
Chalykh and Vasenin ⁸	20	120,000	chlorobenzene	27	12.8	12.8
Chalykh and Vasenin ⁸	20	120,000	ethylbenzene	19	13.7	13.7
Chalykh and Vasenin ⁸	20	120,000	<i>o</i> -xylene	14	8.36	8.36
Chalykh and Vasenin ⁸	20	120,000	toluene	23	15.4, 16.6	15.4, 16.6

^a Values taken from Table II for indicated solvent. Polymer is S109 ($\bar{M}_n = 176,000$).

^b Values read from graphs at a polymer concentration of 30%.

^c Two methods of calculating D were employed.

^d If amyl acetate exhibits the same molecular weight dependence as cyclohexanone (see Fig. 6), then the corresponding value of D at $M = 32,000$ would be 4.27×10^{-7} .

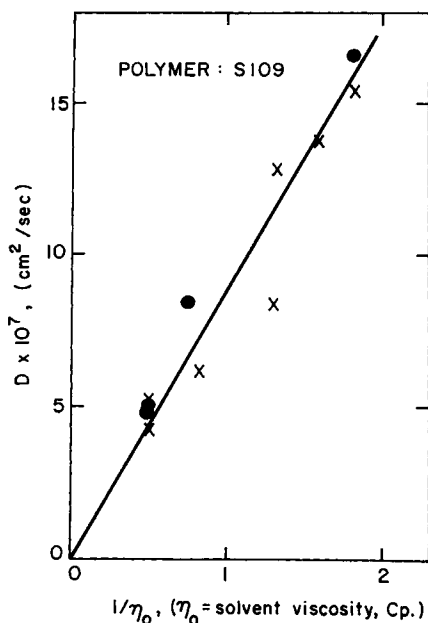


Fig. 4. Diffusion coefficients for cyclic solvents: (●) data obtained with $\omega_{2\infty} = 0$; (X) $\omega_{2\infty} \neq 0$.

Second, we wish to compare numerically the values of D found here with values published by other investigators. Table IV compiles the best data available in the literature on polystyrene for this purpose. The data in no case are directly comparable with ours, as the temperature and molecular weights were not the same. However, the temperature factor, about 5°C difference, is not very significant for a rough comparison. As will be seen later, the molecular weight factor, except for one entry, may not be important at all. Our results compare very well with that of the first two investigators listed, but most of the data presented by the Russian workers are considerably higher than ours. We believe that the narrower concentration limits employed in our experiments make our results more accurate.

The effect of the solvent type on D in any concentration region can be easily hypothesized to reside in three important factors:⁸ the solvent viscosity, the intermolecular forces or thermodynamic interaction between the solvent and the polymer, and the molecular structure (size and shape) of the solvent. In the dilute region, the first and second factors are known to be dominant and the latter is unimportant except as it may affect the first two. In the bulk region, the second and third factors are dominant, with the first unimportant per se. Earlier³³ we termed these as the *hydrodynamic* and *structural* regimes of diffusion. It is not possible to state a priori which, if either of these, are dominant in the concentrated region.

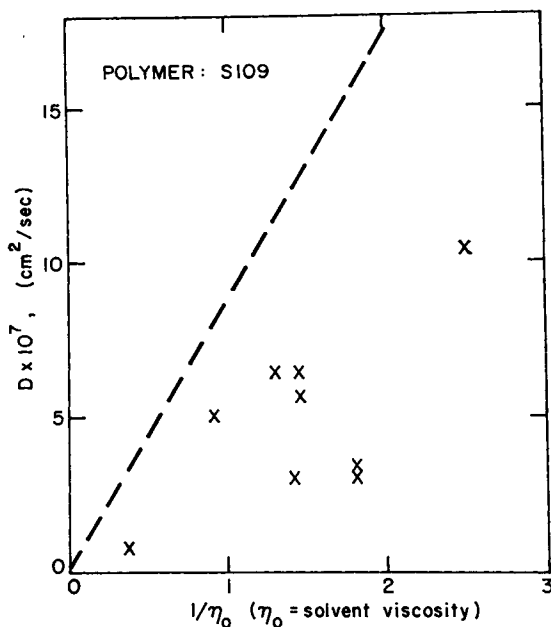


Fig. 5. Diffusion coefficients for noncyclic solvents. All data were obtained with $\omega_{200} \neq 0$. Dotted line is from Fig. 4.

Vasenin⁸ has stated that, at a polymer volume fraction of 0.9, the diffusion coefficients decrease in the order of increasing size and cross-sectional area of the solvent molecule; however, molecular size was not precisely defined. He states that at a polymer volume fraction of 0.1, the diffusion coefficients decrease with increasing solvent viscosity. No quantitative relation is discussed in either case. At a volume fraction of 0.5, he states, no orderly ranking is possible. Our recent work with diffusion through swollen, crosslinked membranes²³ shows a good linear relation between D and $1/\eta_0$. Such a relation may be anticipated outside of the very dilute region if hydrodynamics can be invoked to describe the resistance to relative motion between a polymer chain segment and solvent.³³ In effect, this would mean that the monomeric friction coefficient ζ in eq. (2) is proportional to the solvent viscosity.

To pursue further the issue described above, we selected 14 solvents and made measurements using the polymer S109 the results of which are given in Table II. The initial selection of solvents included only cyclic compounds the results of which are shown in Figure 4 as a plot of D versus $1/\eta_0$. For the most part, the results tend to fall about a straight line. A series of noncyclic solvents were then examined, and they do not even approximately conform to this pattern as can be seen in Figure 5. Interestingly, all of the latter compounds fall below the line for cyclic compounds. Their pattern is complex and cannot be explained simply in terms of molecular size, shape, or polarity. This observation tends to cast

suspicion on the apparent relation observed in Figure 4. It is concluded that probably all three factors cited initially are at issue here, and their effects will be sorted out only after a suitably constructed theory for this region has been developed.

The effect of molecular weight in the concentrated region has not been pursued in a systematic fashion except in the experiments of Ueberreiter.³⁴ He studied the dissolving kinetics of polystyrene and inferred diffusion coefficients from these measurements. The polymer concentration to which this diffusion coefficient belongs is not clear, but it would appear to include the region of interest here. From these measurements he concluded that D is independent of molecular weight.

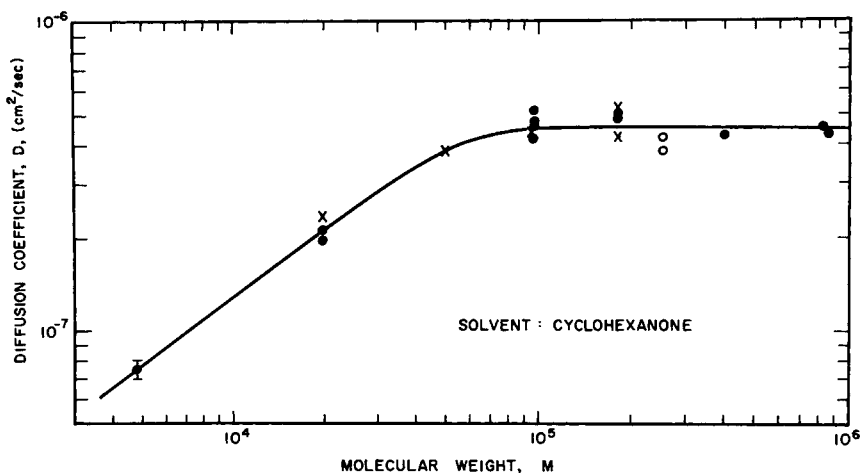


Fig. 6. Diffusion coefficients in concentrated solutions vs. molecular weight of polymer: (●) $\omega_{2\infty} = 0$; (×) $\omega_{2\infty} \neq 0$. Open circles (○) are for the polydisperse Styron 690; their position on the molecular weight axis is located midway between \bar{M}_w and \bar{M}_n for plotting convenience.

Table III contains a sequence of data in cyclohexanone which show the effect of molecular weight. These data are plotted in Figure 6 with a curve drawn to indicate what we believe to be the trend. Although there is some scatter, it definitely appears that D is constant above a molecular weight of about 10^5 . This plot includes data for the polydisperse Styron 690 (the data point is located midway between its \bar{M}_n and \bar{M}_w) and appears to agree well with data on monodisperse polymers. It is reasonable that at some point in molecular weight there should be a plateau, since diffusion coefficients in swollen, crosslinked polymers ($M = \infty$) are in the same range. In fact, we propose that this plateau gives the value one would observe in a swollen polystyrene gel.

Below 10^5 , the data show that D increases with molecular weight, which is a rather startling observation. This part of the curve is based on only six data points, but these are quite consistent and we are forced to believe

that the trend is real. It is perhaps significant to note that the critical molecular weight M_c for bulk polystyrene is 30,000 to 35,000.³⁵ This is the molecular weight where there are two physical entanglements per molecule, and at higher molecular weights an infinite entanglement network results. In solution, M_c varies inversely with the volume fraction of the polymer; so for a 30% solution, M_c would be about 10^6 , which is roughly where the break in D versus M in Figure 6 occurs. This would suggest that the plateau occurs because of the formation of an infinite entanglement network.

Even though the term "mutual diffusion" is applied, it is common to think of the polymer diffusing through stationary solvent in the dilute region and the solvent diffusing through stationary polymer in the bulk region. Naturally, one asks, which is the case in the concentrated region? Before answering this, one must consider the continuity equation and the physical restraints of the experimental apparatus. For example, there can be imposed a steady-state flux of solvent through a swollen, crosslinked polymer membrane when the polymer is absolutely stationary in space.³³ However, in the wedge experiment, the polymer does move since the restraint of constant volume demands that across each plane the flux of polymer and solvent are equal and opposite on a volume basis. It may be argued that in a concentrated solution the solvent flux is by diffusion, but the polymer flux is flow caused by the volume restraint.

Hartley and Crank^{36,37} have discussed this as a general concept in diffusing systems and define intrinsic diffusion coefficients for each species to denote its tendency to diffuse. Within this framework, it is clear that the intrinsic diffusion coefficient of a polymer in the form of an infinite crosslinked network is zero. The same is likely to be so well above M_c since an infinite entanglement network exists; however, in this case the polymer can yield to the volume restraint and flow. Well below M_c , the centers of gravity of the polymer coils may diffuse, but a good deal of interference with one another will be experienced which will increase as the molecular weight increases. This discussion contributes to the idea that the influence of molecular weight on the diffusion coefficient should cease in the neighborhood of 100,000, but makes no suggestion that D should increase with M below this level. The question begs additional experimental evidence and conceptual understanding.

Finally, some conclusions regarding the use of the wedge interferometer are in order. The apparent simplicity of this technique is deceiving, but several pitfalls can be avoided by techniques and procedures described earlier.^{11,13} From the current work, we conclude that low-viscosity materials should not be employed except where adequate precautions against flow and mixing can be ensured.¹³ In addition, extreme variations of D within a given experiment should be avoided by employing narrower concentration limits. If uncertainty exists in the extremes of the diffusion field, then this uncertainty will reflect itself in the D values calculated by eq. (8) across the entire field, and one cannot claim accurate dif-

fusion coefficients even over the middle 70% to 80% of the concentration range, as has been suggested.^{8,13}

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