

## Solvent Effects on Mutual Diffusion in Concentrated Polystyrene Solutions

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### Synopsis

In a previous paper, mutual diffusion coefficients for concentrated solutions of a monodisperse polystyrene in 14 solvents were reported. In this paper, these data are reinterpreted in terms of new thermodynamic data for these solvents. These new results permit evaluation of the activity derivative,  $\partial \ln a_1 / \partial \ln v_1$ , and therefore enable calculation of the diffusional friction coefficient from the mutual diffusion coefficient. The friction coefficient was found to be directly proportional to solvent viscosity to within the experimental errors involved in the combined transport and thermodynamic measurements. The molecular implications of this result are discussed.

### INTRODUCTION

The mutual diffusion coefficient  $D$  for binary mixtures of solvent and polymer depends on concentration in a complex fashion as the entire region of polymer volume fraction  $v_2$  from 0 to 1 is transversed.<sup>1</sup> At the concentration extremes, different factors control as discussed earlier.<sup>1</sup> For *high* molecular weight polymers, there is a maximum in the  $D$  versus  $v_2$  curve in the concentrated solution region which is rather broad and may be regarded as a plateau, with  $D$  independent of concentration. This has been observed for numerous systems<sup>2-8</sup> and generally is believed to exist because of a balance of mobility and thermodynamic factors affecting the mutual diffusion coefficient.<sup>9</sup> In a previous paper,<sup>1</sup> the author reported mutual diffusion coefficients for monodisperse polystyrenes in several solvents which were measured using the microinterferometer method. For one monodisperse polymer, S109 with  $\bar{M}_w = 187,000$ , the plateau  $D$  was obtained for 14 different solvents of varying characteristics. These values, which are shown in Table I, may be regarded as concentration independent, at least in the approximate range of polymer weight fraction from 0.2 to 0.30.

An attempt was made<sup>1</sup> to correlate these data with the viscosity of the solvent  $\eta_0$ . This approach was of interest because of our earlier finding that  $\eta_0 D$  was very nearly a constant for diffusion of solvents in highly swollen network polymers.<sup>10,11</sup> A tentative correlation of this type was observed for the first seven solvents in Table I, which are all cyclic compounds. However, data for the last seven solvents in Table I, which are noncyclic

TABLE I  
Summary of Diffusion and Thermodynamic Parameters

No.	Solvent	$\chi_1$		$\eta$ , cp	$D \times 10^7$ , <sup>(b)</sup> cm <sup>2</sup> /sec	$\phi_1$ <sup>(c)</sup>	$D \phi_1$ (toluene)	
		This work	Boyer <sup>13</sup>				$\phi_1$	$\times 10^7$ , cm <sup>2</sup> /sec
1	Toluene	(0.440) <sup>(a)</sup>	0.440	0.55	15.4	0.0850	1.00	15.4
	Toluene	(0.440) <sup>(a)</sup>	0.440	0.55	16.6	0.0850	1.00	16.6
2	Ethyl benzene	0.475	0.424	0.63	13.7	0.0719	1.18	16.2
3	Chlorobenzene	0.454	0.425	0.76	12.8	0.0798	1.07	13.6
4	<i>o</i> -Xylene	0.484	0.427	0.77	8.36	0.0685	1.24	10.4
5	1,4-Dioxane	0.490	0.465	1.20	6.10	0.0663	1.28	7.82
6	1,2,4-Trichlorobenzene	0.445	—	1.33	8.45	0.0831	1.02	8.64
7	Cyclohexanone	0.472	0.453	2.00	5.20	0.0730	1.16	6.36
		0.472	0.453	2.00	4.22	0.0730	1.16	4.91
		0.472	0.453	2.00	4.94	0.0730	1.16	5.75
		0.472	0.453	2.00	5.00	0.0730	1.16	5.82
		0.472	0.453	2.00	5.05	0.0730	1.16	5.88
8	Methyl ethyl ketone	0.563	0.53	0.40	10.4	0.0389	2.19	22.7
9	Methyl isobutyl ketone	0.620	—	0.55	3.10	0.0175	4.86	15.1
		0.620	—	0.55	3.25	0.0175	4.86	15.8
10	<i>n</i> -Butyl acetate	0.545	—	0.69	6.40	0.0456	1.86	11.9
		0.545	—	0.69	5.62	0.0456	1.86	10.5
11	Acetyl acetone	0.599	—	0.71	3.00	0.0254	3.35	10.0
12	Amyl acetate (primary)	0.534	0.58	0.77	6.40	0.0498	1.71	10.9
13	Ethyl glycol acetate	0.560	—	1.10	5.00	0.0400	2.12	10.6
14	Dimethyl adipate	0.619	—	2.69	0.76	0.0179	4.75	3.61

<sup>a</sup> Assumed value.

<sup>b</sup> Data for monodisperse polystyrene, S109, with  $\bar{M}_w = 187,000$ .

<sup>c</sup> Compared from eq. (6) using  $\psi_2 = 0.25$ .

ketones and esters, showed substantial deviations from this correlation. At the time, it was speculated that the cyclic solvents had in common a similar thermodynamic interaction with the polymer that the others did not share; and, therefore, it would be necessary to adjust the data for this fact before a unique assessment of the mobility factors controlled by the solvent viscosity could be made. To pursue this line of reasoning, we have subsequently evaluated the thermodynamic interactions of each of these solvents with polystyrene. These results are reported here.

### THEORETICAL CONSIDERATIONS

Numerous authors<sup>9,12-16</sup> have recognized the need to factor the mutual diffusion coefficient into parts stemming from mobility and thermodynamic effects. Theories have been constructed from various starting points, but all reduce to the common form<sup>1</sup>

$$D = \frac{kT}{f} \left( \frac{\partial \ln a_2}{\partial \ln \rho_2} \right) \quad (1)$$

where  $f$  is a friction coefficient or mobility-related parameter,  $a_2$  is the polymer activity in solution, and  $\rho_2$  is the polymer mass concentration. The derivative is to be evaluated at constant pressure and temperature. It will prove useful here to use the theory and nomenclature of Bearman<sup>17</sup> because of some conceptual advantages and interpretations it offers when applied to polymeric systems. The pertinent result from this theory is

$$D = \frac{V_1 kT}{\zeta_{12}} \left( \frac{\partial \ln a_2}{\partial \ln v_2} \right) = \frac{V_2 kT}{\zeta_{12}} \left( \frac{\partial \ln a_1}{\partial \ln v_1} \right) \quad (2)$$

where  $\zeta_{12}$  is a frictional coefficient between molecules of types 1 and 2, and  $V_1$  and  $V_2$  are the partial molecular volumes of these species. Either activity derivative may be used because of the equality

$$V_1 \left( \frac{\partial \ln a_2}{\partial \ln v_2} \right) = V_2 \left( \frac{\partial \ln a_1}{\partial \ln v_1} \right) \quad (3)$$

required by the Gibbs-Duhem equation when volume fractions units are employed for concentration.

It is now our hypothesis that for concentrated solutions, including the plateau region, the friction coefficient  $\zeta_{12}$  is proportional to solvent viscosity  $\eta_0$ . However, clearly this will not apply in the limit  $v_2 \rightarrow 1$  and likely breaks down at some point prior to this.<sup>1</sup> Several authors have qualitatively interpreted data along these lines,<sup>4-6</sup> while previously we gave a quantitative proof of it in swollen networks. To explore this hypothesis in the current case, it is necessary to know the activity derivatives so that friction coefficients can be calculated from the  $D$  values in Table I via eq. (2). Ideally, this derivative might be determined by direct experimentation by, say, measuring solvent vapor pressure over solutions of varying concentration. This involves considerable experimental labor,

so an approximate approach which permits a greatly simplified experimental procedure was adopted. This involves assuming that some model equation adequately represents  $a_1$  as a function of  $v_1$  such as the Flory-Huggins equation<sup>18</sup>:

$$\ln a_1 = \ln v_1 + \left(1 - \frac{V_1}{V_2}\right) (1 - v_1) + \chi_1(1 - v_1)^2. \quad (4)$$

This particular model contains the interaction parameter  $\chi_1$  which can be determined by a single suitable measurement. In general,  $\chi_1$  may depend on  $v_1$ , thus necessitating a range of measurements for a full representation; however, for current purposes it will be adequate to neglect such refinements. In this case, eq. (4) can be differentiated to give the required derivative

$$\frac{\partial \ln a_1}{\partial \ln v_1} = 1 - \left[2\chi_1 + 1 - \frac{V_1}{V_2}\right] v_1 + 2\chi_1 v_1^2. \quad (5)$$

Since  $V_1/V_2$  is of the order of  $10^{-3}$  or less for the current situation, this term may be dropped to give finally

$$\frac{\partial \ln a_1}{\partial \ln v_1} \equiv \varphi_1 \cong v_2 (1 - 2\chi_1 v_1). \quad (6)$$

The latter approximation is only restrictive at polymer concentrations much more dilute than involved here. In the limit as  $v_1 \rightarrow 1$ , the approximate equation predicts  $\varphi_1 \rightarrow 0$  where it should go to  $V_1/V_2$  as eq. (5) does.

For the present purposes, it is necessary to find an experimental technique which permits an estimate of  $\chi_1$  so that  $\varphi_1$  can be computed. The next section describes the approach used.

### EXPERIMENTAL EVALUATION OF $\chi_1$

An equilibrium swelling technique similar to that reported by Boyer and Spencer<sup>19</sup> was used here to estimate  $\chi_1$ . This involved preparing cross-linked polystyrene samples and measuring the amount of swelling, or polymer volume fraction  $v_2$ , that occurred at equilibrium upon immersing this sample in a large quantity of the solvent of interest. Absolute values of  $\chi_1$  cannot be deduced by this single measurement unless the crosslink density of the polymer is known.<sup>10,19</sup> However, if  $\chi_1$  is known for at least one solvent, independent evaluation of this additional parameter can be avoided. This requires that all samples have the same crosslink density, which is generally assured if all samples are taken from the same polymer batch. In this approach, the measured equilibrium value of  $v_2$  and the known  $\chi_1$  for the reference solvent are used to calculate the crosslink density from well-known equations.<sup>10</sup> This value of the crosslink density is then employed in these equations to calculate  $\chi_1$  for other solvents from the measured values of  $v_2$ . Toluene was selected as the reference solvent since

its value of  $\chi_1$  for polystyrene is well established<sup>19</sup> at a value of 0.440. Some essential experimental details follow.

Crosslinked polystyrene was prepared by thermally polymerizing a mixture of styrene of 0.326 wt-% divinyl benzene at 105°C for 17 hr in a closed container to avoid evaporation. Specimens from this batch were used in swelling tests. It was necessary to heat the polymer before immersion to avoid crazing with some solvents. Equilibrium was established at 25°C by allowing the samples to remain in the solvent for at least two days. Swelling was determined gravimetrically and converted to a volume basis by known densities. Equilibrium swelling was obtained both from initial dry and final swollen weights and a second dry weight obtained by evaporating the solvent from the specimen in a vacuum oven set at 100°C for two days. Triplicate samples were run; and when excessive deviations were noted between specimens or techniques, repeats were made until a statistically significant result was obtained. Equilibrium polymer volume fractions ranged from 0.11 to 0.34.

The values of  $\chi_1$  found by these experimental and calculational procedures are shown in column 3 of Table I. Values obtained by Boyer and Spencer<sup>19</sup> are shown for comparison where available. The agreement is good in most cases. The deviations that exist are probably indicative of the inherent limitations of the procedure. It is of interest to note that the thermodynamic interaction of the first seven solvents with polystyrene are quite similar since their values of  $\chi_1$  fall in the narrow range of 0.440 to 0.490. The latter seven are much poorer solvents for polystyrene as evidenced by the fact that their  $\chi_1$  extend to values considerably higher than this range.

### CORRELATION OF THE THERMODYNAMICALLY ADJUSTED DIFFUSION COEFFICIENTS WITH SOLVENT VISCOSITY

The mutual diffusion coefficients shown in Table I are independent of concentration at least within the range of 20% to 30% polymer to within the experimental limits of the technique used. However,  $\varphi_1$  is somewhat dependent on concentration in this range, as eq. (6) shows; and, therefore,  $\zeta_{12}$  is concentration dependent to this extent. To facilitate pursuit of the hypothesis stated earlier, we will select a single, midrange concentration,  $v_2 = 0.25$ , to make the comparison among solvents. The values of  $\varphi_1$  shown in Table I were computed at this concentration level.

Rather than deal directly with  $\zeta_{12}$ , we will select a reference solvent, toluene, and adjust the diffusion coefficients for other solvents to this thermodynamic state. The adjusted mutual diffusion coefficient, defined by the left-hand member below, is related to  $\zeta_{12}$  as follows:

$$D \frac{\varphi_1(\text{toluene})}{\varphi_1} = \frac{\text{constant}}{\zeta_{12}} \quad (7)$$

as may be seen from eq. (2) where  $D$  and  $\varphi_1$  apply to the solvent of interest and  $\varphi_1(\text{toluene})$  is the value for toluene. Column 8 of Table I shows the

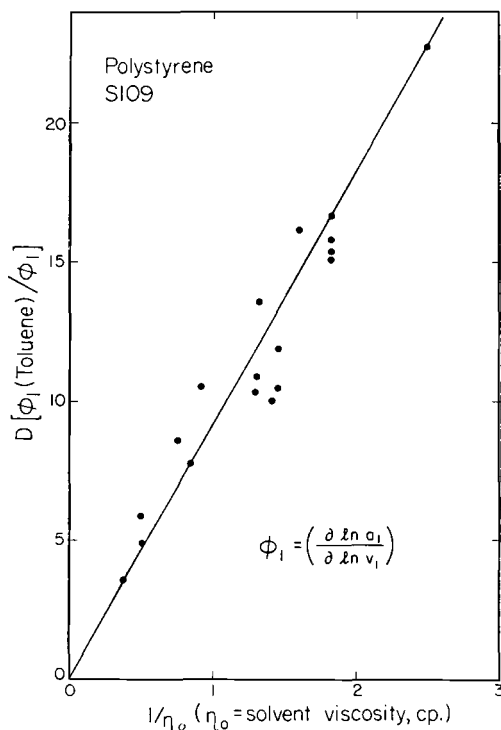


Fig. 1. Correlation of the thermodynamically adjusted mutual diffusion coefficient with solvent viscosity. Data from 14 different solvents are represented. Some data points are for the same solvent as shown in Table I.

ratio of  $\phi_1(\text{toluene})/\phi_1$  for each solvent. Interestingly, this ratio is quite near unity for the first seven solvents but is quite different from unity for the remaining seven. This would explain the previously noted correlation for the cyclic solvents and the lack of a correlation for the latter solvents. The last column gives the thermodynamically adjusted mutual diffusion coefficients. The latter quantity is plotted versus the reciprocal of solvent viscosity in Figure 1. A reasonably good straight-line correlation is observed, which indicates that for these concentrated solutions  $\zeta_{12}$  is proportional to solvent viscosity as suggested earlier. The scatter shown there may be simply a result of the combined experimental errors in determining  $D$  and  $\phi_1$ . Because of the possible errors in both quantities, a more refined analysis to determine any residual dependency on other factors, such as  $V_1$ , is unwarranted.

### SUMMARY

The above observation indicates that solvent diffusion in concentrated polymer solutions involves a hydrodynamic regime.<sup>10</sup> This is also the case in dilute polymer solutions where, after thermodynamic corrections,  $D$  is

known to be inversely proportional to the solvent viscosity.<sup>1</sup> In dilute solutions, it is understood that the resistance to transport arises from the movement of isolated polymer molecules through the solvent as more or less impenetrable particles, or nonfree draining coils, in accordance with Stokes' law.<sup>1,13,18</sup> The polymer molecular weight is a dominant factor since it determines the size of the molecular coil or particle. For concentrated solutions of high molecular weight polymers, the mutual diffusion coefficient is independent of molecular weight.<sup>1</sup> This indicates that the resistance to transport no longer arises from the motion of entire molecules as a discrete particle, which is easily understood from the high degree of coil interpenetration and entanglement that exists in concentrated solutions. Instead, the frictional resistance must be at the segmental or atomic grouping level. Stated another way, the polymer chains shift from nonfree draining to free draining behavior<sup>13,18</sup> as the polymer content increases into the concentrated region.

Diffusion of liquids in highly swollen, crosslinked networks has been interpreted in terms of this free draining concept.<sup>10</sup> A relation similar to Stokes' law applies at the segmental level since the friction coefficient for diffusion is proportional to solvent viscosity. It is interesting to note that the bulk viscosity of concentrated solutions also exhibits a direct proportionality to solvent viscosity once thermodynamic factors are properly considered.<sup>20,21</sup>

Several points regarding the role of solvent viscosity in controlling frictional processes in concentrated polymer systems remain unanswered, however. For example, from the present data it is not possible to say whether the proportionality between the friction coefficient and  $\eta_0$  is exact or just approximate with yet unidentified parameters being operative. It is not known to what concentration level this apparent relation extends. Clearly, at some low level of solvent content,  $\eta_0$  cannot be the most dominant factor.

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### References

1. D. R. Paul, V. Mavichak, and D. R. Kemp, *J. Appl. Polym. Sci.*, **15**, 1553 (1971).
2. M. J. Hayes and G. S. Park, *Trans. Faraday Soc.*, **51**, 1134 (1955); *ibid.*, **52**, 949 (1956).
3. G. Rehage and O. Ernst, *Kolloid-Z. Z. Polym.*, **197**, 64 (1964).
4. A. Ye. Chalykh and R. M. Vasenin, *Polym. Sci. USSR*, **7**, 642 (1964); *ibid.*, **8**, 2107 (1966).
5. V. K. Gromov, A. Ye. Chalykh, R. M. Vasenin, and S. S. Voyutskii, *Polym. Sci. USSR*, **7**, 886 (1966); *ibid.*, **7**, 2319 (1966).
6. M. I. Artsis, A. E. Chalykh, N. A. Khalturinskii, Yu. V. Moiseev, and G. E. Zai-kov, *Eur. Polym. J.*, **8**, 613 (1972).
7. M. Mozisek, *Makromol. Chem.*, **136**, 87 (1970).
8. A. T. Hutcheon, R. J. Kokes, J. L. Hoard, and F. A. Long, *J. Chem. Phys.*, **20**, 1232 (1952).

9. R. E. Pattle, P. J. A. Smith, and R. W. Hill, *Trans. Faraday Soc.*, **63**, 2389 (1967).
10. D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **14**, 2201 (1970); *ibid.*, **15**, 2199 (1971).
11. D. R. Paul and D. H. Carranza, *J. Polym. Sci.*, **41C**, 69 (1973).
12. C. R. Patrick, *Makromol. Chem.*, **43**, 248 (1961).
13. C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1963, Chaps. 4 and 6.
14. J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).
15. S. R. deGroot and P. Mazur, *Non-Equilibrium Thermodynamics*, Interscience, New York, 1962, p. 257.
16. C. Goldstein and R. L. Laurence, *A.I.Ch.E. J.*, **14**, 357 (1968).
17. R. J. Bearman, *J. Phys. Chem.*, **65**, 1961 (1961).
18. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953.
19. R. F. Boyer and R. S. Spencer, *J. Polym. Sci.*, **3**, 97 (1948).
20. D. R. Paul, J. E. St. Lawrence, and J. H. Troell, *Polym. Eng. Sci.*, **10**, 70 (1970).
21. H. F. Mark, N. Bikales, and N. G. Gaylord, *Encyclopedia of Polymeric Science and Technology*, Vol. 13, Wiley, New York, 1970, p. 365.

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