ϵ_{ij}	contact free enthalpy of molecules i and j
ρ	density
ρ_i	density of the pure ith component
ϕ_i	volume fraction before mixing of the ith component (eq 10)
0	superscript denotes the limit at vanishing concentration of polymer

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(10) **Note Added in Proof.** Our most recent experiments indicate that this effect is very large for the mixture of bromobenzene (1)-carbon tetrachloride (2), for which the parameters of eq 47 assume the values $b_0 = 2.11 \times 10^{-2}$ and $b_1 = 0.00$ (546 nm).

Measurement of Diffusion Coefficients of Polymer Solutions Using the Ultracentrifuge

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ABSTRACT: A diffusion experiment in the synthetic boundary cell of an ultracentrifuge yields reproducible values of the diffusion coefficient. For poor and intermediate solvents, these values (uncorrected for the effect of polymer concentration) lead to reasonable values of the Flory–Mandelkern invariant β. Hence, the method in combination with the measurement of either the intrinsic viscosity or the sedimentation coefficient may yield a good estimate of molecular weight. However, for good solvents (highly nonideal solutions), the effect of the polymer concentration cannot be neglected.

In a previous study,[1] we have used a diffusion experiment in the synthetic boundary cell of an ultracentrifuge to measure the refractive increment of polymer solutions. However, these experiments also yielded with good reproducibility the polymer translational diffusion coefficient. While recent developments of quasielastic laser light scattering[2,3] make it possible to measure polymer diffusion coefficients in solution rather rapidly, with accuracies which are claimed to be better than 1%, some problems still remain (effect of dust particles, etc.). Moreover, light-scattering equipment may not be readily available in some laboratories. Thus, it is interesting to see whether our method yields values comparable to the light-scattering results, as well as whether it may yield the basic information which is usually extracted from diffusion data. The main problem is expected to be related to the concentration dependence of the diffusion coefficient. While the theoretical treatments require the diffusion coefficient to be extrapolated to vanishing concentration of polymer, our method yields an integral diffusion coefficient for a boundary between a pure solvent and a polymer solution with a concentration of about 0.004 g/mL.

Experimental Procedure and Results

Polystyrene samples with a narrow distribution of molecular weight obtained from Pressure Chemical Co., Pittsburgh, Pa., were the same ones as those used in our previous studies.[1,4-6] The molecular weight measured by the sedimentation equilibrium method in benzene solutions was found to be 117 000 for sample 4b, 186 000 for sample 1c, 372 000 for sample 3b, and 596 000 for sample 13a. Viscosity of the solvents was measured at 20 °C by the automatic viscometer Fica Viscomatic. The preparation of the solutions and the synthetic boundary experiment were described in detail in our previous publication.[1] All samples were measured in pure benzene, ethyl acetate, and cyclohexane (only sample 4b) as well as in several benzene–cyclohexane mixtures and ethyl acetate–cyclohexane mixtures.

Table I
Diffusion Coefficient of Four Polystyrene Samples in Benzene (1)-Cyclohexane (2) Solvent Mixtures at 20 °C and the Viscosity of the Solvent Mixtures

	$D \times 10^7$ cm²/s for sample				
ϕ_2[a]	4b	1c	3b	13a	η, cP
0.0	4.17	3.26	2.29	1.92	0.662
0.1	4.23	3.42	2.30	1.84	0.646
0.2	4.14	3.33	2.27	1.80	0.638
0.3	4.15	3.26	2.24	1.74	0.637
0.4	4.15	3.37	2.26	1.82	0.644
0.5	4.18	3.24	2.15	1.69	0.660
0.6	3.96	3.12	2.25	1.75	0.686
0.7	3.86	2.96	2.00	1.75	0.724
0.8	3.64	2.88	1.99	1.57	0.781
0.9	3.39	2.64	1.88	1.48	0.866
1.0	3.14				0.985

[a] Volume fraction of component 2.

In Tables I and II we have collected our experimental values of solvent viscosity together with the values of our diffusion coefficients. For those measurements, which were made in duplicate, the difference between the two values reaches 5% only for one pair; for the other measurements the reproducibility is much better.

Discussion

The relation between the diffusion coefficient D and the molecular weight of polymer M is usually written as

$$D = K_{\rm D} M^{-a_{\rm D}} \tag{1}$$

where the constants $K_{\rm D}$ and $a_{\rm D}$ are characteristic of the polymer–solvent system. The exponent $a_{\rm D}$ should be re-

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Table II
Diffusion Coefficient of Four Polystyrene Samples in Ethyl Acetate (1)-Cyclohexane (2) Solvent Mixtures at 20 °C and the Viscosity of the Solvent Mixtures

	$D \times 10^7$ cm²/s for sample						
		1c		3b			
ϕ_2[a]	4b	1st set	2nd set	1st set	2nd set	13a	η, cP
0.0	6.23	5.05	4.89	3.31		2.45	0.463
0.1	6.05	4.54	4.71	3.21	3.28	2.38	0.463
0.2	5.81	4.55	4.66	3.05	2.98	2.45	0.470
0.3	5.73	4.36	4.31	2.89	2.80	2.20	0.482
0.4	5.28	4.11	4.03	2.76	2.78	2.15	0.503
0.5	4.95	3.92	4.07	2.53	2.67	1.99	0.530
0.6	4.72	3.68	3.67	2.39	2.38	1.92	0.567
0.7	4.27	3.54		2.31	2.28	1.81	0.620
0.8	4.08	3.09	3.00	2.10		1.53	0.692
0.9	3.69	2.73		1.79	1.71	1.49	0.802
1.0	3.14						0.985

[a] Volume fraction of component 2.

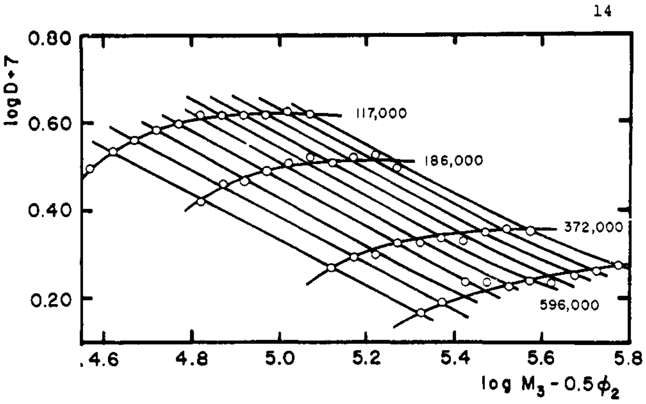

Figure 1. Zimm-type plot of the dependence of the diffusion coefficient on the molecular weight and composition of the solvent for polystyrene in benzene (1)–cyclohexane (2) solvent mixtures. The curves are marked by the molecular weight of the sample.

lated to the viscometric Mark–Houwink–Sakurada exponent a_η as

$$a_\eta + 1 = 3a_D \quad (2)$$

We first tried to analyze our diffusion data using eq 1. To improve the reliability of the correlation we employed the Zimm-type plot:[7] log D was plotted vs. (log $M + k\phi_2$), where ϕ_2 is the volume fraction of the second component of the solvent mixture and k is an arbitrary constant. We expected to obtain straight lines at constant composition of the solvent mixture with a slope yielding the exponent a_D. Actually, the dependences were not quite straight. When we forced them to be straight lines, the derived exponents were not related to a_η as required by eq 2. (The values of a_η for the same samples in ethyl acetate–cyclohexane mixtures and in benzene were published previously.[6])

In our second attempt, we correlated the experimental points using curves. The resulting plots are presented in Figures 1 and 2. The correlation is within the experimental error. The curves for good solvents (pure benzene; mixtures of benzene and a small amount of cyclohexane) are slightly concave upward, while those for poor solvents (pure ethyl acetate; mixtures of ethyl acetate and a small amount of cyclohexane) bend slightly down. For intermediate solvents, the lines are essentially straight. We interpret this behavior as a result of neglecting the effect of concentration when evaluating the diffusion coefficient.

The standard treatment[8] of the concentration dependence of the diffusion coefficient leads to the expression

$$D = D_0[1 + (2A_2M - k_f)c + \ldots] \quad (3)$$

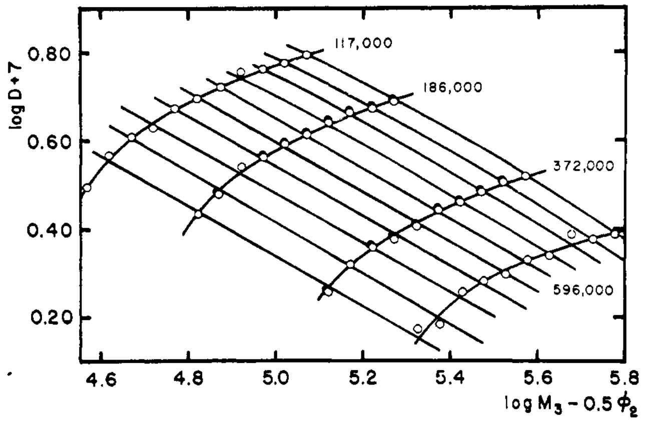

Figure 2. Zimm-type plot of the dependence of the diffusion coefficient on the molecular weight and composition of the solvent for polystyrene in ethyl acetate (1)–cyclohexane (2) solvent mixtures. The curves are marked by the molecular weight of the sample.

where the subscript zero denotes a value extrapolated to zero concentration of polymer. A_2 is the second virial coefficient, M is the molecular weight of polymer, and c is its concentration. k_f is a coefficient related to the concentration dependence of the friction coefficient; it is a positive quantity. Thus, for good solvents, the value of D at higher concentration is larger than D_0; the effect increases with increasing molecular weight. For poor solvents, k_f dominates over $2A_2M$, and D is decreasing with increasing concentration. For intermediate solvents, D is essentially independent of concentration. The curvature as observed in our Figures 1 and 2 is fully compatible with these predictions based on eq 3.

To test the above interpretation further, we have used our values of diffusion coefficients for the calculation of the Flory–Mandelkern invariant β. Flory and Mandelkern[9] have predicted that the ratio of the equivalent hydrodynamic radius of polymer molecules applicable for translational movement (diffusion) to the radius applicable for rotary movement (viscosity) should be independent of the nature of the polymer–solvent system. It follows that the quantity β, defined by eq 4, should be a universal constant.

$$\beta \equiv \phi^{1/3}P^{-1} \equiv D_0\eta M^{1/3}[\eta]^{1/3}/kT \quad (4)$$

Here, η is the viscosity of the solvent, $[\eta]$ is the intrinsic viscosity of the polymer, and kT has its usual meaning. Φ is the universal viscosity constant of Flory; P is an analogous constant for diffusion.[10] Once the value of β has been established, eq 4 may serve for the calculation of

Table III
Flory-Mandelkern Invariant $\beta \times 10^{-7}$ of Polystyrene in Mixed Solvents

	in B(1)-CH(2)[b]	in EA(1)-CH(2)[b]					
	sample	sample					
			1c		3b		
ϕ_2[a]	1c	4b	two sets		two sets		13a
0.0	1.266	1.096	1.128	1.094	1.080		1.025
0.1	1.296	1.094	1.052	1.090	1.092	1.116	1.046
0.2	1.237	1.087	1.097	1.123	1.086	1.061	1.135
0.3	1.199	1.120	1.099	1.086	1.079	1.046	1.072
0.4	1.242	1.090	1.097	1.074	1.093	1.100	1.114
0.5	1.209	1.089	1.114	1.156	1.070	1.126	1.098
0.6	1.181	1.108	1.116	1.112	1.083	1.074	1.133
0.7	1.148	1.081	1.158		1.117	1.104	1.143
0.8	1.157	1.129	1.101	1.069	1.100		1.039
0.9	1.119	1.132	1.066		1.020	0.981	1.084
1.0		1.049					
B[b]		1.243	1.266		1.345		1.481

[a] Volume fraction of component 2. [b] B designates benzene, CH cyclohexane, and EA ethyl acetate.

molecular weight from measured values of D_0 and $[\eta]$.

The values of $[\eta]$, needed for the calculation of β, were reported previously[6] for the same samples of polystyrene in the same mixtures of ethyl acetate and cyclohexane, in benzene, and, for the sample 1c, also in mixtures of benzene and cyclohexane. The values of β are collected in Table III. For the solvents with medium solvent power (the same solvents for which the log D vs. log M plot was linear), we have found $\beta = (1.10 \pm 0.05) \times 10^7$. This is in excellent agreement with the value $\beta = (1.08 \pm 0.04) \times 10^7$ obtained from the relations reported by McDonnell and Jamieson[2] for polystyrene with narrow distribution of molecular weights dissolved in tetrahydrofuran and measured by the light-scattering method. It is also in good agreement with the value $\beta = (1.16 \pm 0.05) \times 10^7$ calculated by Flory[10] from a large number of older diffusion measurements. (The value given by Flory[10] is 2.5×10^7; the difference is due to his reporting of $[\eta]$ in units of dL/g.) However, all of the above values are lower than the theoretical value $\beta = 1.29 \times 10^7$, which was calculated for unperturbed coils, for which $\Phi = 2.87 \times 10^{23}$ (ref 11) and $P = 5.11$ (ref 10). We do not know the reason for this descrepancy.

For poor solvents, our value of β is a few percent lower than the value obtained for the intermediate solvents in agreement with eq 3, according to which D decreases with increasing concentration in poor solvents. For good solvents, β appreciably increases with the improving thermodynamic quality of the solvent and with increasing molecular weight. For our highest molecular weight sample 13a in the very good solvent benzene, the increase was about 35%. Such behavior should be expected according to eq 3.

Conclusions

The reported method of measuring the diffusion coefficient of polymers produces values which need not be corrected for the concentration dependence if the polymer is dissolved in an intermediate solvent. When a poor solvent is used, the error is still acceptably small. For such solvents, the method (combined with the measurement of intrinsic viscosity) may yield good estimates of the molecular weight.

However, when the solvent is good and the molecular weight is high, an appreciable error may be committed if the correction for the concentration dependence is neglected. Moreover, even if the neglected correction is small for measurements in intermediate solvents, it may be significant enough to foul any attempt for obtaining the parameters of eq 1.

The method may prove to be useful for biochemical samples, which are usually not strongly nonideal. For such samples, the diffusion coefficient may be combined with the sedimentation coefficient, and molecular weight may be calculated from the well-known Svedberg equation.

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