

Diffusion in Infinitely Dilute Polystyrene Solutions

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Synopsis

The validity and range of applicability of the Kirkwood-Riseman theory is examined by utilizing diffusivity data taken on infinitely dilute polystyrene solutions. The predictions of the theory are found to be in good agreement with diffusivity data obtained on the polystyrene-cyclohexane system at the theta temperature. It is concluded that diffusivity data which are in substantial disagreement with predictions based on the Kirkwood-Riseman approach are unreliable because of mixing effects which take place in a wedge interferometer when organic solvent-polymer systems are used. An extension of the Kirkwood-Riseman theory to polymer diffusion under nontheta conditions is presented and this modification satisfactorily represents diffusivity data when excluded volume effects are important.

INTRODUCTION

The Kirkwood-Riseman theory^{1,2} of transport processes in polymer solutions provides a convenient method for predicting the translational diffusion coefficient at infinite dilution under theta conditions. However, since this theory is based on an approximate model of polymer transport and since an *a priori* value of the draining parameter can not be assigned, experimental confirmation of the validity of the theory is required. Experimental verification of the Kirkwood-Riseman expression for the translational diffusion coefficient is of particular interest in light of the theoretical study of Zwanzig et al.³ and the recent experimental investigation of Paul et al.⁴ Zwanzig et al.³ discovered singularities in the solution of the equations in the Kirkwood-Riseman scheme which lead to negative translational diffusion coefficients. This inconsistency is presumably a consequence of the approximate nature of the model, namely, treating segments as point sources of friction. Paul et al.⁴ presented diffusivity data for polymer solutions which, as is evident below, cannot reasonably be explained within the framework of the Kirkwood-Riseman theory.

The objective of this paper is to examine the validity and range of applicability of the Kirkwood-Riseman theory of polymer diffusion. We first compare the predictions of the theory with diffusivity data for the polystyrene-cyclohexane system at the theta temperature where the complications of the excluded volume effect are absent. Diffusivity data taken on samples with a

narrow molecular weight distribution are considered so as to reduce the effect of difficulties associated with sample polydispersity. In addition, diffusion data taken on polystyrene-solvent systems under nontheta conditions are considered, and the applicability of the wedge interferometer for the measurement of diffusion coefficients of mixtures of polymers and organic solvents is discussed. Finally, we construct a straightforward extension of the Kirkwood-Riseman theory which can be used to predict diffusion coefficients at infinite dilution for polymer-solvent mixtures under nontheta conditions.

THEORY

The Kirkwood-Riseman equation for the translational diffusion coefficient at infinite dilution is simply²

$$D_0 = \frac{kT}{n\zeta} \left(1 + \frac{8}{3}X \right) \quad (1)$$

$$X = \frac{2^{1/2}n^{1/2}\zeta}{\mu_0 a (12\pi^3)^{1/2}} \quad (2)$$

where a is the effective bond length of the chain, n is the number of effective bonds or segments in a chain, ζ is the translational friction coefficient of a segment, and μ_0 is the solvent viscosity. The draining parameter X is a measure of the hydrodynamic interaction between segments. The intrinsic viscosity data of Krigbaum and Flory,⁵ taken under theta conditions, show there is no draining effect, and, thus, the Kirkwood-Riseman theory has significance only in the nonfree-draining limit where there is a very large hydrodynamic interaction between segments ($X = \infty$). Furthermore, Yamakawa² has presented evidence for the absence of a draining effect under nontheta conditions; and, hence, we assume here that there is no draining effect for flexible chains irrespective of the nature of the solvent. Consequently, for $X \rightarrow \infty$, eq. (1) reduces to

$$(D_0)_\theta = \frac{0.196 kT}{\mu_0 \left(\frac{\langle R^2 \rangle_0}{M} \right)^{1/2} M^{1/2}} \quad (3)$$

where $\langle R^2 \rangle_0$ is the mean-square end-to-end distance of the unperturbed chain and M is the polymer molecular weight. This result is based on an approximate solution of an integral equation; and, therefore, the numerical constant in eq. (3) is not exact. However, an exact solution to the integral equation⁶ for the case $X = \infty$ shows that the error is less than 2%, and this refinement is not important for the present study.

The above results are of course valid only at the theta temperature for a given polymer-solvent mixture, but it is possible to construct a straightforward extension of the Kirkwood-Riseman theory in the following manner. The translational friction coefficient at infinite dilution under nontheta conditions, f_0 , can be related to the friction coefficient for an unperturbed chain, $(f_0)_\theta$, by introducing the expansion factor α_f :

$$f_0 = (f_0)_\theta \alpha_f \quad (4)$$

Hence, we can relate the diffusion coefficient in the presence of excluded volume effects to the Kirkwood-Riseman result as follows:

$$D_0 = \frac{(D_0)_\theta}{\alpha_f}. \quad (5)$$

Kurata and Stockmayer⁷ have concluded that the difference between α_f and α_S , the linear expansion factor of the polymer chain based on the mean-square radius of gyration, is insignificant; and so we introduce the approximation

$$\alpha_f = \alpha_S. \quad (6)$$

Now, $\alpha_S \geq 1$, except for very poor solvents, and it follows that the Kirkwood-Riseman result provides an upper bound for diffusion coefficients in infinitely dilute polymer-solvent systems for all solvents of practical importance:

$$D_0 \leq (D_0)_\theta. \quad (7)$$

Values of α_S can be obtained by using the two-parameter theory which is valid for dilute solutions of linear flexible-chain polymers for high molecular weights of ordinary interest. The two-parameter scheme requires that α_S be given by an equation of the form

$$\alpha_S = \alpha_S(A, B, M) \quad (8)$$

where

$$A = \left[\frac{\langle R^2 \rangle_0}{M} \right]^{1/2} \quad (9)$$

and B is a measure of the effective volume excluded to one segment by the presence of another. For a given polymer, both A and B depend, in general, on the temperature and on the nature of the solvent, but it has been found that the solvent effect on A is usually insignificant for nonpolar polymers.^{2,7,8} For this study, we adopt the Yamakawa-Tanaka⁹ expression for α_S because of its apparent consistency with experimental data:

$$\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \quad (10)$$

$$z = \left(\frac{3}{2\pi} \right)^{3/2} \frac{M^{1/2}B}{A^3}. \quad (11)$$

Consequently, if A and B are known for a particular polymer-solvent system, then eqs. (3), (5), (6), (10), and (11) can be used to predict D_0 for a given temperature and polymer molecular weight.

RESULTS AND DISCUSSION

Table I contains a comparison between diffusion data (D_0) taken on the polystyrene-cyclohexane system at the theta temperature (approximately 35°C) and the predictions of the Kirkwood-Riseman theory $[(D_0)_\theta]$ as given by eq. (3). We have assumed that the polymer fractions are sharp enough so that the average diffusion coefficient which is measured is, with negligible error, equivalent to the diffusion coefficient for a homogeneous polymer with $M = M_w$, where M_w is the weight-average molecular weight of the heteroge-

TABLE I
Diffusion Data for Polystyrene-Cyclohexane System Under Theta Conditions^a

$M \times 10^{-3}$	$D_0 \times 10^7,$ cm ² /sec	$\frac{D_0}{(D_0)_\theta}$	Reference
21	8.97	0.77-0.89	10
110	4.20	0.83-0.96	
200	3.05	0.81-0.94	
670	1.66	0.81-0.93	
2700	0.84	0.82-0.95	
208	3.082	0.91	11
465	2.225	0.98	
1010	1.436	0.93	
1890	1.14	0.93-1.1	12

^aWhere more than one average molecular weight is reported, M_w is included in this table.

neous polymer. Some substantiation of this hypothesis is given for two of the experimental studies.^{10,11} Values of the parameter A obtained by light-scattering measurements were utilized in eq. (3). When estimated corrections are introduced for the polydispersity of the polymer sample, reported values of A typically range from 0.66×10^{-8} cm to 0.76×10^{-8} cm.^{11,13-16} In Table I, the unperturbed dimension measured by Cowie and Cussler¹¹ is used to calculate the ratio $D_0/(D_0)_\theta$ for their data, whereas the extreme values of A were utilized to obtain a range for $D_0/(D_0)_\theta$ for the other two investigations.

It is evident from Table I that there appears to be no systematic deviation

TABLE II
Diffusion Data for Various Polystyrene-Solvent Systems

Solvent	$M \times 10^{-3}$	$D_0 \times 10^7,$ cm ² /sec	$\frac{D_0}{(D_0)_\theta}$	Reference
Methyl ethyl ketone	20.8	22.5	1.1	17
	33.0	16.0	0.99	
	111	8.1	0.92	
	200	5.95	0.90	
	392	3.95	0.84	
	507	3.30	0.80	
	670	2.90	0.81	
	2700	1.30	0.73	
	8700	0.70	0.70	
	3500	1.1	0.70	
Toluene	44	7.5	0.79	18 ^a
	140	4.0	0.75	19
	520	1.9	0.68	
	950	1.1	0.54	
	2700	0.70	0.57	
	130	3.0	0.54	20 ^a
Cyclohexanone	50	8.9	3.3	4
	180	5.0	3.6	
	402	2.7	2.9	
	130	0.89	0.61	20 ^a

^aData taken on polymer samples with unreported heterogeneity.

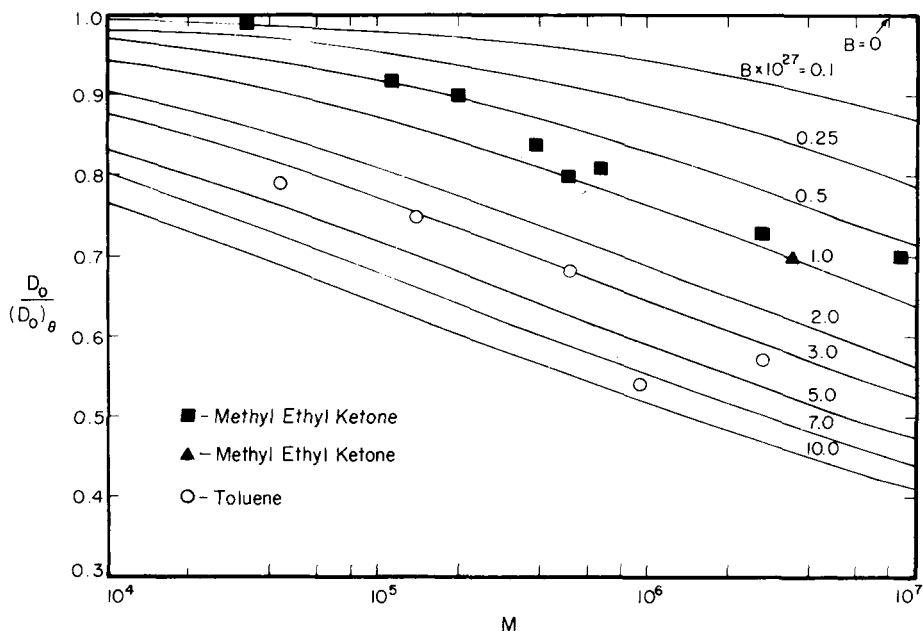


Fig. 1. Comparison of theoretical predictions with experimental data: (■) methyl ethyl ketone data of King et al.¹⁷; (▲) methyl ethyl ketone data of Tsvetkov and Klenin¹⁸; (○) toluene data of Meyerhoff and Nachtigall.¹⁹

with molecular weight of the experimental results from the Kirkwood-Riseman theory, and the assumption of a negligible draining effect appears to be valid, at least for flexible-chain polymers and molecular weights of ordinary interest. Furthermore, the experimental results serve as an effective verification of the Kirkwood-Riseman result since the discrepancy between theory and experiment is quite close to the estimated experimental error in determining the unperturbed dimension and the diffusivity, which is probably of the order of 7–10%. Hence, the available data show that the Kirkwood-Riseman theory quite accurately describes polymer-solvent diffusion at infinite dilution under theta conditions.

In Table II, we have included diffusion results for polystyrene-solvent systems under nontheta conditions. Most of the data were taken using samples with narrow molecular weight distributions, but a few results on samples of unknown polydispersity are included for comparison purposes. The Kirkwood-Riseman prediction, $(D_0)_\theta$, was calculated using $A = 0.670 \times 10^{-8}$ cm which is the value derived by Kurata and Stockmayer⁷ from intrinsic viscosity data and which is in the lower end of the light scattering results. It is evident that all of the data except those of Paul et al.⁴ obey the inequality of eq. (7), within experimental error. Not only are the data of these investigators in substantial disagreement with predictions based on the Kirkwood-Riseman approach, but they differ by more than a factor of five from the results of Vallet.²⁰ Comparison of the toluene data of Vallet with those of Meyerhoff and Nachtigall¹⁹ shows a discrepancy of about 40%. Hence, it would appear that the reliability of the diffusion experiment of Paul et al.⁴ is suspect, and there is no question as to any inadequacy of the Kirkwood-Riseman theory.

These investigators have suggested that mixing effects may be important in a wedge interferometer; and, indeed, this appears to be the major source of error. We have conducted diffusion experiments on the polystyrene-1,2,4-trichlorobenzene system and have obtained values of the diffusivity which are approximately one half of those reported by Paul et al.⁴ These experimental data are still open to question since we have no guarantee that we have eliminated mixing effects. Clearly, the wedge interferometer experiment is sensitive to the initial mixing which takes place at the start of an experiment. For systems for which water is the solvent, it is possible to make this effect negligible.²¹ However, it has yet to be shown that this can be done for systems involving organic solvents where surface effects cause much more severe mixing problems. The mixing effect can be reduced by avoiding the use of the pure solvent in the wedge, but the degree of the reduction of the effect is not known. Consequently, we conclude that diffusivity data taken on organic solvent-polymer systems using a wedge interferometer are suspect, and more testing must be done using systems with known diffusivities before such an apparatus can be used with confidence.

Finally, in Figure 1, we compare the toluene and methyl ethyl ketone data with the predictions of the extension of the Kirkwood-Riseman theory presented above. This figure illustrates the molecular weight dependence of $D_0/(D_0)_\theta$ for a range of values of B and for $A = 0.670 \times 10^{-8}$ cm. The diagram represents polystyrene-solvent diffusion at infinite dilution and at a temperature of approximately 25°C. If lines were drawn through the experimental points, their shapes would be in reasonable agreement with the shapes of the theoretical curves presented in the diagram (when allowance is made for the scatter in the data). Furthermore, a value of $B = 0.7 \times 10^{-27}$ cm³ could be assigned to the methyl ethyl ketone data and a value of B slightly over 3×10^{-27} cm³ appears to represent the toluene data satisfactorily. The parameter B can not be obtained directly from experiment but must be deduced from a combination of experiments and the equations of the two-parameter theory. Berry and Casassa⁸ report a value of $B = 0.76 \times 10^{27}$ cm³ for methyl ethyl ketone and $B = 4.95 \times 10^{-27}$ cm³ for toluene, whereas Yamakawa² concludes that a value of B slightly over 2×10^{-27} cm³ represents available toluene data adequately. It is evident, therefore, that the above modification of the Kirkwood-Riseman theory satisfactorily describes available diffusivity-molecular weight data with reasonable values of B and, hence, should provide a useful method for the estimation of D_0 for polymer-solvent mixtures under nontheta conditions.

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