EFFECT OF MOLECULAR ASSOCIATION ON OSMOTIC PRESSURE AND DIFFUSION IN DILUTE POLYMER SOLUTIONS

By

Kit Leung Yam

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ABSTRACT

EFFECT OF MOLECULAR ASSOCIATION ON OSMOTIC PRESSURE AND DIFFUSION IN DILUTE POLYMER SOLUTIONS

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Polymer molecules in solution often associate with one another via secondary binding forces (such as hydrogen bonds) to form larger polymer molecules. Examples may be found in many biopolymers and synthetic polymers consisting of proton-donating and proton-accepting pairs. However the influence of these associated complexes on solution properties is still not well understood, for at least two reasons. First, existing theories are incapable of describing the behavior of these systems and, second, very few relevant data are available in the literature.

In this work, expressions for the osmotic pressure and the diffusion coefficient are derived for open associating systems. The associating systems are treated as pseudo-binary systems--the two components being solvent molecules and polymer molecules with number average molecular weight of the multimer mixture.

The osmotic pressure π^* is expressed as

$$\frac{M_1 \pi^*}{\rho R T} = \Psi_1 + A_2^* M_1 \rho + \ldots$$

and the diffusion coefficient D^* is expressed as

$$D^* = D_o \left\{ \Psi_2 + [\ 2 A_2^* M_1 / \Psi_1 - (k_s + 2 V_{po}) \Psi_2] \rho + \dots \right\}$$

where ρ and M_1 are the mass concentration and the unimer molecular weight of polymer, respectively. A_2^* is the second virial coefficient of the multimer mixture. Ψ_1 and Ψ_2 (both dimensionless groups) are functions of ρ , M_1 and the association equilibrium constant K. The partial specific volume of polymer at infinite dilution, V_{po}, can be obtained from density experiments, and the friction parameter, k_s, can be estimated from the Pyun-Fixman theory.

The model predicts that the initial slope of $\pi^*/\rho RT$ versus ρ is

$$(A_2^*)_{obs} = A_2 - K/M_1^2$$

which differs from its nonassociating counterpart A_2 by K/M_1^2. Similarly, the initial slope of D^* versus ρ is

$$(k_d^*)_{obs} = k_d - K/M_1$$

which differs from its nonassociating counterpart k_d by K/M_1.

Predictions from these expressions agree well with osmometry data obtained from the literature and with diffusivity data measured in this laboratory, for polyethylene glycol in benzene. The effect of association is most prominent at low concentrations and increases progressively with decreasing molecular weight. Its magnitude is governed by the dimensionless group $K\rho/M_1$.

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The completion of this dissertation would have been impossible without the constructive suggestions of my major professor, Dr. Donald K. Anderson. More than this, I thank him for helping me to develop the skills and confidence to meet the challenge of the future.

I am also indebted to my other committee members, Dr. Eric A. Grulke, Dr. Krishnamurthy Jayaraman, and Dr. Frederick Horne for their support and encouragement throughout the course of this work.

FOREWORD

This dissertation consists of two parts. Part One provides a summary for the essential findings of this work. It was prepared in the form for publication. Part Two provides a more detailed description of the work.

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PART ONE

Abstract

Expressions for the concentration dependence of osmotic pressure and diffusion coefficient in dilute polymer solutions are derived in this work for open associating systems. Predictions from these expressions are in good agreement with the experimental data of polyethylene glycol in benzene obtained from our laboratory and from the literature. The effect of association increases with decreasing molecular weight and is governed by the dimensionless group $P = K\rho/M_1$.

1. INTRODUCTION

The objective of this work is to study the effect of intermolecular association on osmotic pressure and diffusion coefficient of dilute polymer solutions.

Polymer molecules in solution often associate with one another to form larger molecules under favorable conditions.[1,2] The resulting associated complexes may be classified, based on the nature of intermolecular forces, into hydrogen-bonding complexes, polyelectrolyte complexes, stereocomplexes, and charge-transfer complexes.[3] The extent of association is affected by the mechanism of association, the chemical structures of polymer and solvent, solute concentration, temperature, and pressure.

The behavior of associating polymer solutions is still not well understood, for at least two reasons. First, there is a lack of sufficient and reliable experimental data available in the literature. Second, existing theories, such as the Flory-Huggins and the two-parameter theories,[4] are incapable of describing the behavior of these systems; their applications are valid only for nonassociating, nonelectrolyte systems.

Yet there exist many biopolymers and synthetic polymers which form associated complexes in solution,[3] and the formation of these complexes can greatly influence the solution properties. For example, osmotic pressure, an important colligative property, may be strongly affected by molecular association. A plot of reduced osmotic pressure versus polymer concentration generally displays a linear relation. In fact this linear relationship is the basis for molecular weight determination.[5] However, if the polymer associates, this linear relationship is no longer valid (especially in the very dilute concentration range) and molecular weight determination based on linear extrapolation may be in serious error.[6] Other solution properties such as viscosity and diffusion coefficient are also influenced. Hence, there is a need for a better understanding of these systems.

In this paper we formulate theoretical expressions for the concentration dependence of osmotic pressure and diffusion coefficient for associating polymer-solvent systems. Since these expressions depend on the type of association, we limit our study to the systems which obey the so-called "open association" model.[2] However, the procedures described below may also be applied to other types.

First, we derive the concentration dependence of osmotic pressure for open association. This expression describes the behavior of a pseudo-binary system--the two components being the solvent molecules, and the polymer molecules with number average molecular weight of the multimer mixture. Second, the osmotic pressure expression is used to derive an expression for diffusion coefficient.

To test the validity of the model we compare theoretical predictions of osmotic pressure and diffusion coefficient with experimental data. Polyethylene glycol (PEG) in benzene is used. Mutual diffusion coefficients for this system, with molecular weight ranges from 440 to 12600, were measured in our laboratory.

II. MOLECULAR ASSOCIATION

When considering colligative properties and diffusion, associating polymer-solvent systems are more difficult to study than nonassociating systems. Unlike nonassociating systems, they cannot always be considered to be binary but must be treated as multicomponent systems which consist of unimers, dimers, trimers, etc., with molecular weight distributions that change with concentration. In order to construct a model to describe their behavior, a prior knowledge of the mechanism of association must be assumed and its validity tested with experimental data.

For simplicity, we restrict our study to polymer-polymer association in inert solvents, although association can also occur between polymer-solvent and solvent-solvent molecules. We further restrict it to open association because this model is obeyed by many synthetic polymers and is simple to construct.[21]

Open association is a consecutive association in which successively higher multimers (dimers, trimers, etc.) are formed one step at a time:

$$B_1 + B_1 \rightleftarrows B_2 \ , \quad K = K_2$$

$$B_1 + B_2 \rightleftarrows B_3 \ , \quad K = K_3$$

$$\cdots\cdots\cdots\cdots$$

$$B_1 + B_{i-1} \rightleftarrows B_i \ , \quad K = K_i$$

$$\cdots\cdots\cdots\cdots$$

$$B_1 + B_{n-1} \rightleftarrows B_n \ , \quad K = K_n \qquad (1)$$

where B_i represents i-mer, K_i represents the association equilibrium constant for the formation of i-mer and n takes all positive integers up to infinity.

If we assume K_i is independent of molecular size (for example, in the case of end-group association), and thus $K_1 = K_2 = \ldots = K$, we obtain

$$C_i = K^{i-1} C_1^{\,i} \tag{2}$$

and

$$KC_1 = C_2/C_1 = C_3/C_2 = \ldots \text{ etc.} \tag{3}$$

where C_i is the molar concentration of i-mer. KC_1 is a dimensionless group whose value ranges from 0 to 1: $KC_1 = 0$ corresponds to no association ($C_2 = C_3 = C_4 = \ldots = 0$), and $KC_1 = 1$ corresponds to the maximum allowable association when all multimers have the same concentration ($C_1 = C_2 = C_3 \ldots$, etc.).

With the above description of the model and the relation $M_i = iM_1$, some useful relations can be derived:[6]

$$\Psi_1\{\rho\} = M_1/M_a = \frac{2}{1 + \xi} \tag{4}$$

$$KC_1 = 1 - \Psi_1 \tag{5}$$

$$C_i/C_p = (1 - KC_1)(KC_1)^{i-1} \tag{6}$$

$$M_w/M_n = 1 + KC_1 \tag{7}$$

where

$$\xi = \sqrt{1 + 4P} \tag{8}$$

$P = K\rho/M_1$ (9)

M_a = apparent polymer molecular weight = C_p/ρ (10)

M_w/M_n = polydispersity of the multimer mixture (11)

C_p = true molar concentration of polymer solute

$$= \sum_{i=1}^{\infty} C_i \qquad (12)$$

Equations (4) through (7) are expressed in terms of measurable quantities: the polymer mass concentration ρ, the association constant K, and the unimer molecular weight M_1. The apparent molecular weight M_a, is equivalent to the number average molecular weight of multimer mixture and can be readily calculated from Equation (4) once M_1, K and ρ are known.

It is noteworthy to point out the similarities between open association and stepwise polymerization. In fact, Equations (4) through (7) can be obtained from the appropriate expressions for stepwise polymerization, by substituting KC_1 for the fraction of conversion.[7] The molecular distribution can be identified with the Schultz-Zimm distribution.[8] Since $0 \leq KC_1 \leq 1$ and according to equation (7), the polydispersity is bounded between $1 \leq M_w/M_n \leq 2$.

III. MODEL DEVELOPMENT

A. Osmotic Pressure

As mentioned in Section II, open associating systems are simply heterogeneous systems with molecular weight distribution governed by Equation (4). In the following, the osmotic pressure expression of heterogeneous systems is tailored for describing these systems.

In a dilute solution containing heterogeneous polymer molecules, the osmotic pressure π may be expressed as:[4]

$$\frac{\pi}{\rho RT} = \frac{1}{M_n} + A_2\rho + \ldots \tag{13}$$

and the second virial coefficient A_2 is given by

$$A_2 = \sum w_i w_j A_{ij} \tag{14}$$

where M_n is the number-average molecular weight, w_i the weight fraction of polymer molecule i, and A_{ij} the interaction between the pair of polymer molecules i and j at infinite dilution. According to the two-parameter theories, A_{ij} is a function of the excluded volume z and the ratio of molecular weights of molecules i and j.[9,10]

To adapt Equation (13) for associating systems, M_a is substituted for M_n, and A_2^* for A_2:[2,6]

$$\Pi = \frac{M_1\pi^*}{\rho RT}$$

$$= \Psi_1\{\rho\} + A_2^* M_1 \rho + \ldots \tag{15}$$

is defined for convenience. The superscript * denotes open association. Ψ_1 is a function of ρ.

A_2^* is a function of association. Recently Tanaka and Solc[8] have suggested that it may be approximated by the second virial coefficient of a monodisperse polymer, with number-average molecular weight of the multimer mixture. Furthermore, if the Mark-Houwink relationship ($A_2 = K' M^{-\alpha}$) is assumed,[11,12] we can incorporate the molecular weight dependence of A_2^* into Equation (15). However, this leads to a rather complicated diffusivity expression. Moreover, our calculations show that the osmometry data used in this work are relatively insensitive to the molecular weight dependence of A_2^*. Hence, an A_2^* independent of concentration is assumed for each molecular weight sample.

For $K = 0$, M_a and A_2^* reduce to M_1 and A_2 (the second virial coefficient of unimer), respectively; and Equation (15) reduces to the expression for nonassociating systems. Differentiating Equation (15) with respect to ρ and evaluating the result at $\rho = 0$, we obtain the observed second virial coefficient

$$(A_2^*)_{obs} = A_2 - \frac{K}{M_1^2} \tag{16}$$

for associating systems. Note that $(A_2^*)_{obs}$ differs from its nonassociating counterpart by K/M_1^2.

B. Diffusion Coefficient

The concentration dependence of the mutual diffusion coefficient for a nonassociating dilute polymer solution can be expressed by the series expansion:[13]

$$D = Do\ (1 + k_d\ \rho + . . .) \tag{17}$$

where

$$k_d = 2\ A_2\ M - k_s - 2\ V_{po} \tag{18}$$

and

$$V_p = V_{po}\ (1 + a\ \rho + . . .) \tag{19}$$

$$f = f_o\ (1 + k_s\ \rho + . . .) \tag{20}$$

Here Do is the diffusion coefficient at infinite dilution, V_p the partial specific volume of polymer, and f the friction coefficient.

If associating systems are treated as pseudo-binary systems (i.e. use the apparent molecular weight, M_a, to represent the average molecular weight of the multimer mixture), Equation (15) may be used to obtain the chemical potential of the solvent, μ_s:[4]

$$\mu_s - \mu_s^{\,o} = -\pi^* \bar{V}_s \tag{21}$$

and the mutual diffusion coefficient may be derived from the relation:[13,14]

$$D = \frac{1 - V_p \rho}{N_a f}\ \frac{M}{M_s}\ \rho_s \left(\frac{\partial \mu_s}{\partial \rho} \right)_{T,P} \tag{22}$$

where N_a is the Avogadro's number; M_s $\bar{V}_s$ and ρ_s are the molecular weight, the molar volume and the mass concentration of solvent, respectively. Using Equation (15) and Equations (19) through (22), we obtain the mutual diffusion coefficient D^* for associating systems as

$$D^* = Do \left\{ \Psi_2 + \left[2 A_2^* M_1 / \Psi_1 - \left(k_s + 2 V_{po} \right) \Psi_2 \right] \rho + \ . \ . \ . \right\} \tag{23}$$

where

$$\Psi_2 = \frac{1 + \xi}{2\xi} \tag{24}$$

Both Ψ_1 and Ψ_2 are functions of concentration and open association. For K = 0, Equation (23) reduces to Equation (17).

Differentiating Equation (23) with respect to ρ and evaluating the result at ρ=0, we obtain

$$(k_d^*)_{obs} = k_d - K/M_1 \tag{25}$$

Note that $(k_d^*)_{obs}$ differs from its nonassociating counterpart by K/M_1.

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IV. EXPERIMENTAL

Diffusion coefficients were measured in our laboratory using a Mach-Zehnder interferometer.[15,16] Monodisperse polyethylene glycol (PEG) polymer samples ($M_w/M_n < 1.06$) were purchased from Polymer Laboratories, Inc., Massachusetts; these samples were used without further purification. Solution temperature was controlled at 25.0 ± 0.1°C. The accuracy of the interferometer was tested by comparing the diffusion coefficients for several aqueous sucrose solutions with those reported by Gosting and Morris;[17] average deviation was found to be less that 1%. However, PEG/benzene system has a smaller refractive index difference compared to the sucrose/water system, and the diffusion coefficients reported in this work (some of them represent the average values of two or three runs) are estimated to be within 4%.

V. RESULTS AND DISCUSSION

A. Osmotic pressure data

The vapor pressure osmometry data of Elias[18] for PEG in benzene is chosen here for studying the effect of molecular association. Infrared spectroscopic measurements by Langbein[19] had shown that intramolecular hydrogen bonds existed between the hydroxyl end-groups and the ether groups in this system; later, Elias found[18,20] that intermolecular association also existed and the data could be quantitatively explained by the open association model.

The value of K is estimated first from the osmometry data. According to Equation (16), if the dependence of A_2 on M_1 is weak, a plot of $(A_2^*)_{obs}$ versus $1/M_1^2$ should yield a straight line, with slope equal to -K. In fact the osmometry data of Elias fit such a straight line quite well, and thus the slope provides a good initial value of K. Next, Equation (15) and the method of least squares are used to obtain the final values of K = 11000 cc/mole (which agrees with the value estimated by Elias using a different approach[18]) and A_2^*. The values of A_2^* are presented in Table I.

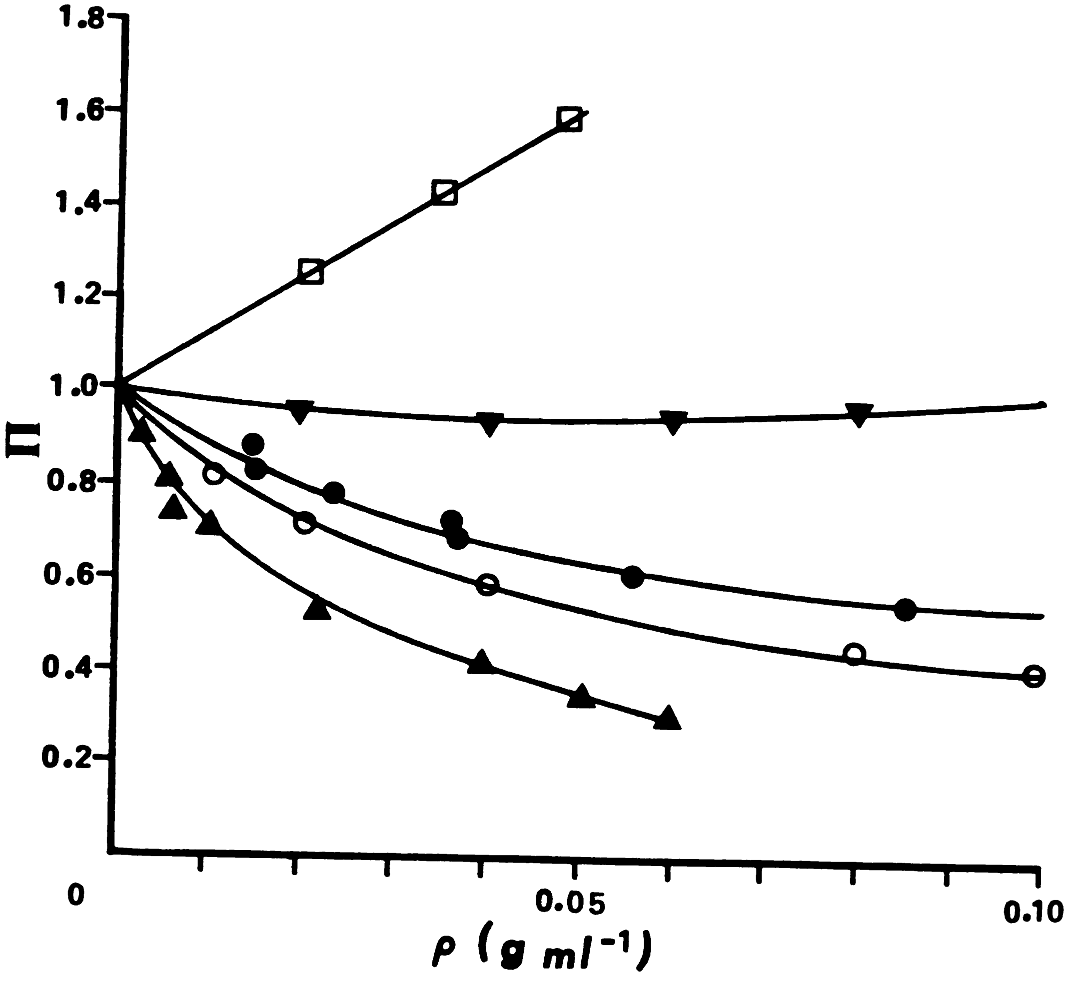
Table I. Values of A_2^* (mole ml/g^2) estimated from the osmometry data of Elias.[18] For comparison, (A_2) is the second virial coefficient calculated from two-parameter theories.[4]

M_1	A_2^*	(A_2)
208	-0.0095	-0.0027
409	-0.0011	0.0011
594	0.0005	0.0018
1518	0.0020	0.0023
6000	0.0022	0.0019

The performance of the model is shown in Figure 1. The effect of association is more prominent at low concentrations and increases progressively with decreasing molecular weight. This behavior is well described by the model.

Figure 1. Concentration dependence of Π for PEG in benzene at 25°C. Data taken from Elias et al.[18]

(□) M_1=6000; (▼) M_1=1518; (●) M_1=594;
(○) M_1=409; (▲) M_1=208.
——— predictions from Equation (15).


1.8
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B. Diffusivity data

As shown in Section III, the prediction of $D(\rho)$ in dilute solutions requires the evaluation of A_2^*, K, V_{po}, D_o and k_s. The first two terms have already been estimated from the osmometry data, and V_{po} can be obtained from density experiments. D_o and k_s can be estimated from the two-parameter scheme suggested by Vrentas and Duda[21]: D_o from the modified Kirkwood-Riseman theory and k_s from the Pyun-Fixman theory (version II),[22] because they seem to be the best methods available at the present time. The short-range interferences, A, for PEG/benzene system at 25°C is given by[11]

$$A = \left[\frac{\langle R^2 \rangle_o}{M_1} \right]^{0.5} = 7.9 \times 10^{-9} \text{ cm} \qquad (26)$$

where $\langle R^2 \rangle_o$ is the unperturbed mean-square end-to-end distance. The long-range interferences are estimated indirectly from the empirical Mark-Houwink intrinsic viscosity relationship:[4,21]

$$[\eta] = K_v M_1^{\beta} = 0.063 M_1^{0.64} \qquad (27)$$

where $[\eta]$ is the intrinsic viscosity. The values of K_v and β are obtained from curve fitting the raw data of Rossi and Cuniberti[23] using the method of least squares. In addition, to adapt the two-parameter scheme to associating systems, the apparent molecular weight M_a is substituted for the unimer molecular weight M_1 in calculating the necessary parameters.

Several investigators had shown that the Kirkwood-Riseman theory provided reasonable predictions for $(D_o)_\theta$, the translational diffusion coefficient at infinite dilution under theta conditions[24, 25, 26, 27]. Furthermore, Vrentas and Duda extended this theory for predicting D_o under nontheta conditions[27]

$$D_o = \frac{(D_o)_\theta}{\alpha_s}$$

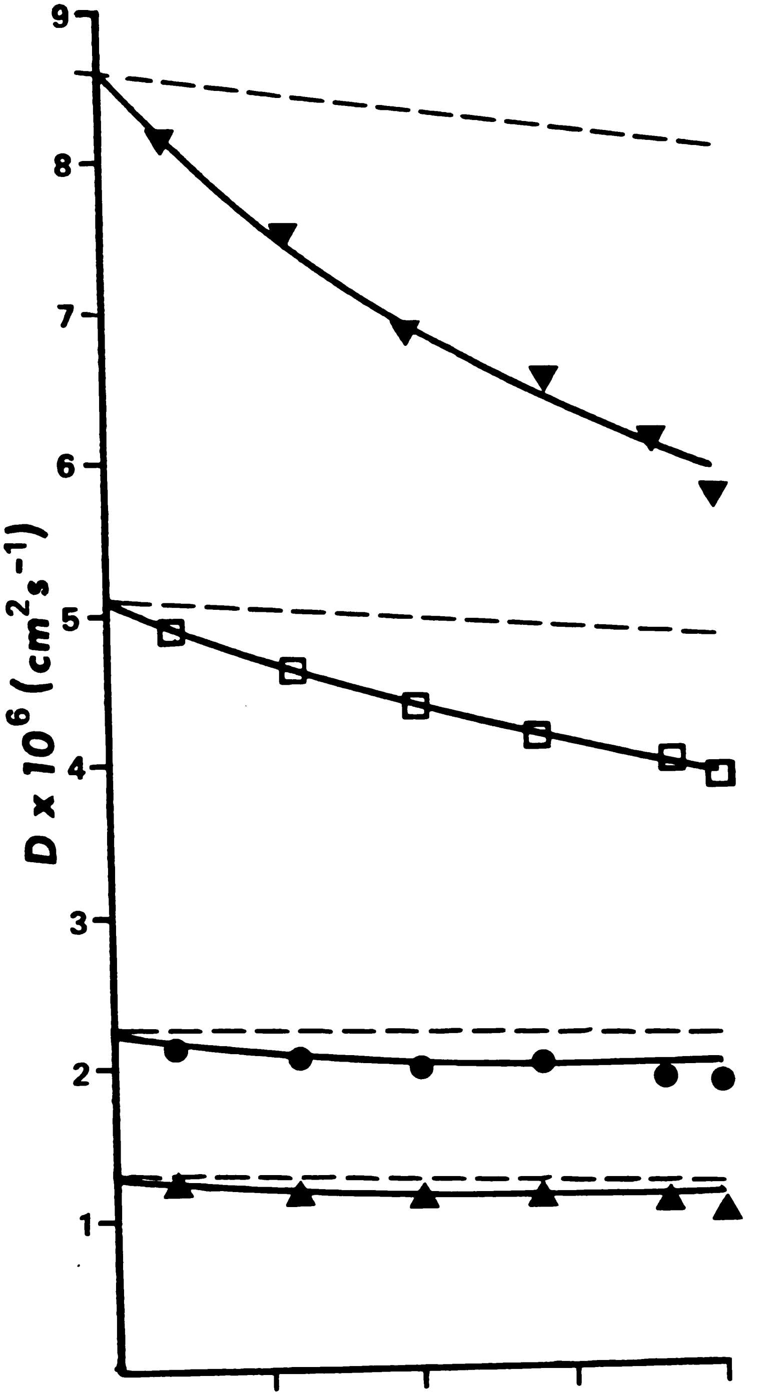
$$= \frac{0.196\ k\ T}{\alpha_s\ \eta_s\ A\ M^{0.5}} \tag{28}$$

where k is the Boltzmann's constant, η_s is the viscosity of solvent, and α_s is the expansion factor relating the perturbed and the unperturbed mean-square radii of gyration.

Mutual diffusion coefficients for four PEG samples in benzene at 25°C were measured using a Mach Zehnder interferometer. The concentration dependence is shown in Figure 2. The experimental D_o is found by extrapolation using the model and the method of least squares. They are found to be in good agreement with the predictions (see Table II). The molecular weight dependence of D_o is shown in Figure 3 along with a least squares fit to the relation

$$D_o = G\ M_1^{\gamma} = 2.64 \times 10^{-4}\ M_1^{-0.57} \tag{29}$$

Figure 2. Concentration dependence of diffusion coefficient for PEG in benzene at 25 °C. Experimental data: (▼) M_1=440; (□) M_1=960; (●) M_1=4250; (▲) M_1=12600.
——— predictions from the association model (Equation (23)); ------- predictions from the nonassociation model (Equation (17)).


D x 10^6 (cm^2s^-1)
9
8
7
6
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4
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2
1
0
0.005
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0.020
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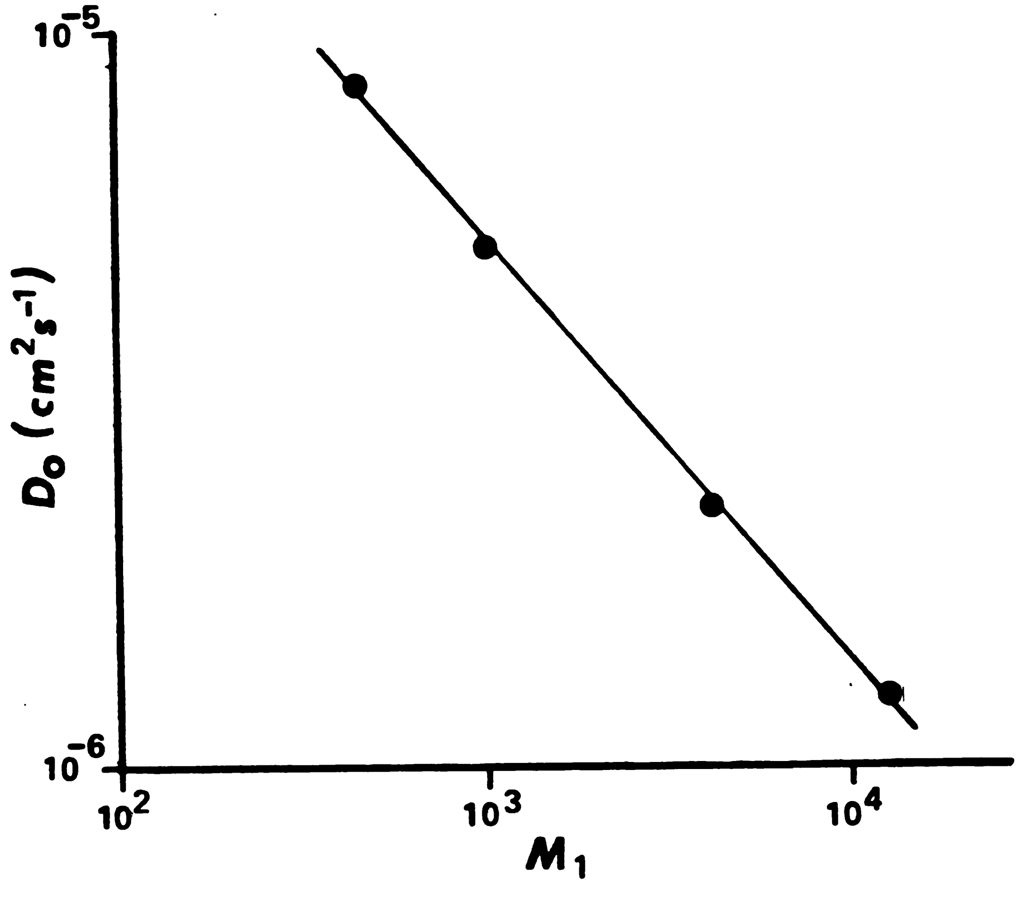

Figure 3. Plot of D_o versus M_1 for PEG in benzene at 25 °C.

Flory suggested the exponents γ and β may be related by[28]

$$\gamma = (\beta + 1) / 3 \tag{30}$$

Thus γ may be calculated to be 0.55, using $\beta = 0.64$ from Equation (27), and this value agrees reasonably well with $\gamma = 0.57$ from Equation (29). However, larger differences are observed for some systems[11,29] and more experimental data are needed to determine the validity of this relation.

Table II. Comparison of D_o (cm^2/sec) from the modified Kirkwood-Riseman theory (Equation (28)) with D_o from experiment for PEG in benzene at 25°C.

M_1	M_w/M_n	D_o(theory)	D_o(exptl)	D_o(exptl)/ D_o(theory)
440	< 1.09	8.31×10^{-6}	8.58×10^{-6}	1.03
960	< 1.06	5.30×10^{-6}	5.05×10^{-6}	0.95
4250	< 1.03	2.31×10^{-6}	2.20×10^{-6}	0.95
12600	< 1.04	1.28×10^{-6}	1.25×10^{-6}	0.98

The performance of the association model is shown in Figure 2. $K = 11000$ cc/mole is used, and the values of A_2^* are taken from the osmometry data (see Table III). The only adjustable parameter used to fit the data is λ of the Pyun-Fixman theory (version II).[22] For our data $\lambda = 0.88$ provides the best fit. (This compares to $\lambda = 0.86$ used by Vrentas and Duda to fit the diffusivity data of polystyrene in cyclohexane.)[22] Agreement between experimental and predicted values is good.

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Table III. Values of A_2^* (mole ml/g^2) used in calculating the concentration dependence of diffusion coefficient in Figure 2. For comparison, (A_2) is the second virial coefficient calculated from the two parameter theories.[4]

M_1	A_2^*	(A_2)
440	-0.0010	0.0013
960	0.0012	0.0022
4250	0.0021	0.0020
12600	0.0018	0.0016

As for osmotic pressure, the effect of association is found to be the strongest for low molecular weights. In fact, for the polymer sample $M_1 = 440$, $(k_d^*)_{obs}$ can roughly be equated to $-K/M_1$ (see Equation (25)). As molecular weight increases, the virial term and friction term also become important. For comparison, the predictions using the nonassociating model are also shown in Figure 2.

At theta conditions and when the contributions of k_s and V_{po} are negligible, Π reduces to Ψ_1 and D^*/D_o reduces to Ψ_2. Since Ψ_1 decreases more rapidly with increasing concentration than Ψ_2, osmotic pressure is affected more strongly compared to diffusion coefficient by association. (As P approaches infinity, Ψ_1 and Ψ_2 approach 0 and 0.5, respectively.)

Some $D(\rho)$ curves from the literature[6,30,31] display minima, even at dilute concentrations. The diffusion rate first decreases sharply with increasing concentration and then attains an almost constant value or passes through a minimum. This behavior can be explained at p

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least qualitatively by the association model if the polymer molecules associate with one another in a thermodynamically good solvent. Equation (23) suggests that, at very dilute concentrations, association dominates and causes the diffusion rate to decrease with increasing concentration; at higher concentrations, the thermodynamic term dominates (assuming that the hydrodynamic and volumetric terms are relative small) and causes the diffusion rate to increase with concentration.

VI. CONCLUSION

The association model and the two parameter theories provide good predictions for both the osmometry and diffusivity data for PEG in benzene. $(A_2^*)_{obs}$ and $(k_d^*)_{obs}$ differ from their nonassociating counterparts only by K/M_1^2 and K/M_1, respectively. The effect of association increases with decreasing molecular weight and is governed by the dimensionless group $P = K_\rho/M_1$.

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PART TWO

CHAPTER I

INTRODUCTION

The purpose of this work is to study the effect of association on the concentration dependence of osmotic pressure and diffusion coefficient in dilute polymer solutions.

The term "association" is defined here as a rapid equilibrium between unimers (unassociated molecules) and multimers (associated molecules). Many synthetic polymers and biopolymers in solution are capable of associating with one another to form larger molecules via secondary binding forces such as hydrogen bonds. Several studies [B-13, B-18, B-37] have indicated that the extent of association depends on the type of association, the chemical structures of polymer and solvent, molecular weight, polydispersity, concentration, and temperature.

An associating system is a multi-component system consisting of polymer unimers, polymer multimers, and solvent molecules. The distribution of unimers and multimers may change drastically with polymer concentration, depending on the type of association. Consequently,

association can greatly influence those solution properties which are functions of molecular size. Moreover, if the molecular weight of a polymer is to be determined accurately, the possibility of association must be investigated--if the polymer associates, traditional methods for molecular weight determination (such as linear extrapolations of osmotic pressure in dilute solutions) should not be used.

In spite of its importance, relatively few studies have been reported for association in polymer solutions. There exists no satisfactory theory for describing the solution properties of these systems. In addition, the lack of pertinent data in the literature makes the situation even more unfavorable.

The first systematic investigation of associating macromolecules was conducted by Elias [B-18]. He studied a large number of polymer-solvent pairs (both natural and synthetic polymers) under various conditions and was successful in describing the thermodynamic properties of some of these systems using association models.

Only recently has the effect of association on diffusion been studied. Lin [B-35] measured the osmotic pressures and the diffusion coefficients for two forms of polytetrahydrofuran. The two ends of these polymer types had different functional groups attached--one the methyl a

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group and the other the hydroxyl group. Methylethylketone (MEK) and bromobenzene (BB) were chosen as the solvents. Based on an association model, he derived an expression for the osmotic pressure

$$\frac{\pi}{\rho R T} = \frac{1}{(M_n)_{app,\theta}} + A_2\rho_p + A_3\rho_p^2 + \ldots \qquad (1\text{-}1)$$

and an expression for the diffusion cofficient

$$D_{obs} = D^o \chi_{asso} (1 + k_d^m \rho_p + \ldots) \qquad (1\text{-}2)$$

where he defined $(M_n)_{app,\theta}$ as the "apparent number average molecular weight of polymer molecules in associating solutions under theta condition" and k_d^m as the "linear concentration dependence constant of the average diffusion coefficient of all diffusing associated and non-associated species". He concluded that the hydroxyl endgroups could cause the polymer molecules to associate strongly with one another.

However, Lin's work can be questioned in several respects. First, he used a membrane osmometer to measure osmotic pressures and his polymer samples had molecular weights so low (one of them was determined by him to be as low as 2500) that the use of this kind of osmometer is not recommended. It is very difficult to prevent molecules of molecular weight smaller than 20,000 from leaking through the membrane (see Chapter III). Consequently, faulty data might have been obtained by him. However, if leakage of polymer molecules through the membrane did occur, the actual molecular weights for these polymer samples would be even smaller and the effect of association greater than those predicted by him.

Second, Equations (1-1) and (1-2) are oversimplified. It has long been recognized that the second virial coefficient is dependent on molecular weight [B-4, B-7, B-9, B-57]. Justification must be provided for Lin's assumption of constant A_2^* and k_d^m.

Third, the parameters χ_{asso} and k_d^m in Equation (1-2) are devoid of physical meaning (because they are expressed in complicated summation terms) and are obtained almost solely from curve fitting the diffusivity data. Actually, the concentration dependence of diffusion coefficient, k_d, is governed by three factors [B-49, B-57]--the thermodynamic, hydrodynamic, and volumetric effects. The volumetric effect is usually relatively insignificant, and the thermodynamic and hydrodynamic factors can be estimated from the two-parameter theory [B-50].

In this work a different approach is used to study the effect of association on polymer solutions. New expressions for the osmotic pressure and the diffusion coefficient, based on the open association model, are derived. These expressions include the molecular weight dependence of the second virial coefficient, and are expressed in terms of physical quantities which can be obtained easily. Predictions from these expressions are compared with the osmometry and the diffusivity data of polyethylene glycol (PEG) in benzene.

CHAPTER II

MOLECULAR ASSOCIATION

A. General Background

Under favorable conditions, polymer molecules in solution can form intermolecular complexes with solvent molecules or with other polymer molecules [B-36, B-46]. Examples for association of polymer molecules with solvent molecules are the binding of iodine to amylose, the binding of counterions to polyions, the association of enzymes with substrates, inhibitors, etc. Examples for association of polymer molecules with other polymer molecules are the nonspecific association of cationic and anionic polymers, the formation of hemoglobin and various enzymes from separate protein subunits, the interaction of antigens with antibodies, etc.

Furthermore, intermolecular complexes in polymer solutions may be divided, based on the nature of binding forces, into four classes: polyelectrolyte complexes, hydrogen-bonding complexes, stereocomplexes, and charge transfer complexes. Numerous examples for each class have been compiled by Tsuchida and Abe [B-46].

The formation of intermolecular polymer complexes has been studied under many names [B-18]--association, self-association, aggregation, polymerization, multimerization, complex formation, denaturation, sociation, supersociation, agglomerization, etc. The association between polymer molecules in an inert solvent is treated exclusively in this work. The term "association" or "multimerization" is defined here as a rapid equilibrium between unimers (unassociated molecules) and multimers (associated molecules). Thus an associated solution consists of a mixture of unimers, dimers, trimers, etc. The term "monomer" is avoided here because it is more properly used to designate the molecule from which the polymer is formed. Instead, the term "unimer" is used to represent a polymer molecule which is not associated with another polymer molecule via a secondary binding force.

Association is a function of polymer concentration. As polymer concentration increases, the polymer molecules are packed more closely together and, consequently, associate with one another to a greater extent. The size and the number of polymer molecules may change drastically depending on the type of association.

Two groups of methods are commonly used to study association: "the group specific methods" and "the molecule specific methods" [B-18]. Examples for the group specific methods are infrared spectroscopy, nuclear magnetic resonance, ultraviolet, etc. As its name implies, these methods can be used to determine the structure of a "group" and the type of interaction that can occur between this group and another group. On the other hand, examples for the molecule specific methods are osmometry, light scattering, ultracentrifugation, viscometry, gel permeation, chromatography, diffusivity, etc. As its name implies, these methods look at the "molecule" as a whole and can be used to determine the characteristics of polymer molecules such as the molecular weight. In general, the group specific methods should not be used to study the association of a polymer which have only a few associogenic groups (groups that are capable of associating). These associogenic groups can escape being detected because they constitute such a small part of the polymer molecule. In contrast, the molecule specific methods are the prime choices for studying association because the drastic change in apparent molecular weight (due to association) can be easily detected.

B. Types of Association

When studying association, a physical model is assumed a priori and tested for consistency with experimental data.

An important consideration in constructing an association model is to determine whether the number of associogenic groups are dependent on the size of the polymer molecules. "End-to-end association" is the kind in which the number of associogenic groups per molecule is constant, regardless of the length of the polymer. An example is the association of two polymer molecules via associating endgroups. On the other hand, "segment-to-segment association" [B-17, B-18, B-44] is the kind in which the number of associogenic groups increases proportionally with the length of the polymer.

End-to-end association is discussed exclusively here. It is assumed that the unimers and the multimers are distinguishable only in size, but not in shape and chemical properties.

1. Open association

There are two basic types of end-to-end association--open association and closed association. "Open association" is one in which all types of multimer are present, and successively higher multimers are formed one step at a time:

$$B_1 + B_1 \rightleftarrows B_2 , \quad K = K_2$$

$$B_1 + B_2 \rightleftarrows B_3 , \quad K = K_3$$

. . . .

$$B_1 + B_{i-1} \rightleftarrows B_i \ , \qquad K = K_i$$

. . . .

$$B_1 + B_{n-1} \rightleftarrows B_n \ , \qquad K = K_n \tag{2-1}$$

where B_i represents i-mer. Note that the open association model does not exclude associations such as

$$B_2 + B_2 \rightleftarrows B_4 \ , \quad K = K' \tag{2-2}$$

because the molar concentration

$$C_2 = K{C_1}^2 \tag{2-3}$$

$$C_4 = K'{C_2}^2 = K^3{C_1}^4 \qquad (\text{for } K' = K) \tag{2-4}$$

which is identical to Equation (2) in Part One for the open association model.

An analogy can be made between open association and stepwise polymerization. In stepwise polymerization, each polymer formed can react further with a monomer to form a larger polymer via a chemical bond, in a manner similar to Equation (2-1). Thus the mathematics for open association and stepwise polymerization are closely related. For example, the mole fraction of the i-mer in the multimer mixture (on a solvent free basis) is

$$C_i/C_p = (1 - KC_1)(KC_1)^{i-1} \tag{2-5}$$

and the polydispersity is

$$M_w/M_n = 1 + KC_1 \tag{2-6}$$

for open association. On the other hand, the mole fraction of x-mer (where x is the degree of polymerization) and the polydispersity for stepwise polymerization can be obtained from Equations (2-5) and (2-6) respectively, simply by substituting the fraction of conversion (of stepwise polymerization) for the dimensionless group KC_1 [B-41].

Another type is the "closed association" in which only unimers and n-mers are present:

$$nB_1 \rightleftarrows B_n \qquad (2\text{-}7)$$

Of course, combinations of open association and closed association are possible. However, only open association is treated in this work because this type of association is very useful for describing the behavior of many synthetic and natural polymers [B-18]. Some of the characteristics of open association are discussed below.

As shown in Part One, the behavior of open association can be expressed in terms of the dimensionless group $P = K\rho/M_1$. Both K and M_1 can be obtained from osmotic pressure measurements.

The dimensionless parameter Ψ_1 (see Equation (4) in Part One) is the ratio of the unimer molecular weight to the apparent molecular weight. It is related directly to the extent of association and to the reduction of molecules in solution (due to association). A plot of Ψ_1 versus P is shown in Figure 2-1. Ψ_1 decreases most rapidly in the region near infinite dilution, indicating that the effect of association is most prominent in this region.

It is interesting to see how the i-mers are distributed when the apparent molecular weight is equal to that of unimer, dimer, etc. A plot of molecular weight distribution versus apparent molecular weight is shown in Figure 2-2. C_i/C_p is the mole fraction of i-mer in the multimer mixture (on a solvent free basis). For low apparent molecular weights, the distribution tends towards the small i-mers; for high apparent molecular weights, the i-mers are more evenly distributed.

2. Dimerization

Selecting an appropriate association model is so critical that several promising candidates should be tested with experimental data.

Here the behavior of the dimerization model and the open association model are compared. The dimerization model is represented by

$$B_1 + B_1 \rightleftarrows B_2 \tag{2-8}$$

and the apparent molecular weight is

$$\Psi_1' \equiv M_1 / M_a' = 0.5 + 1 / (1 + \zeta) \tag{2-9}$$

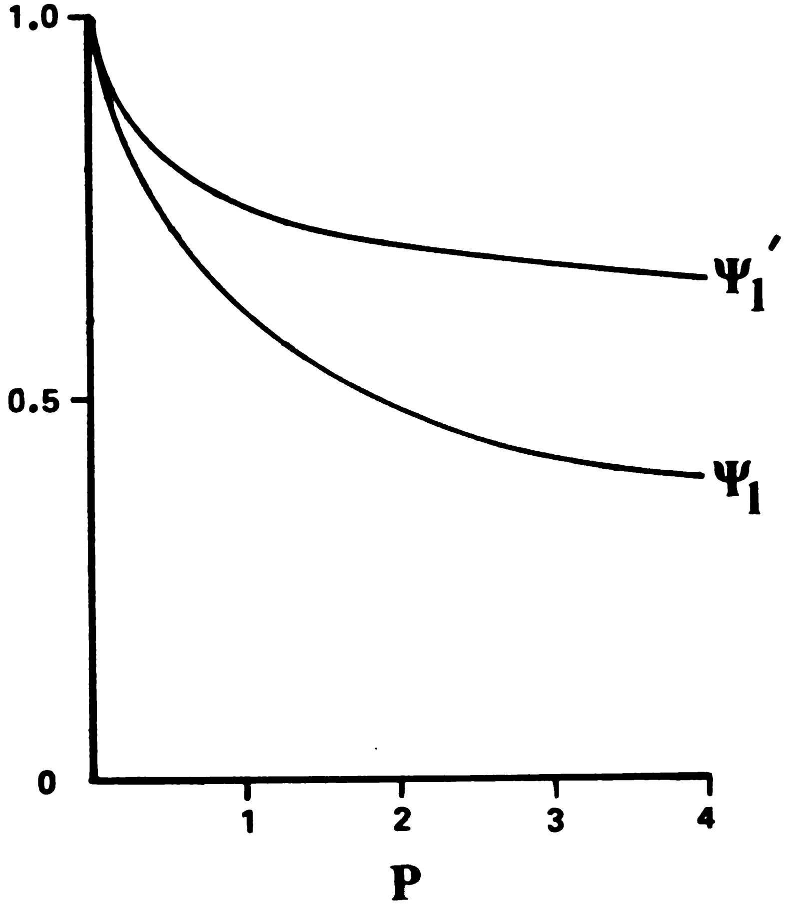

Figure 2-1. Ψ_1 and Ψ_1' versus P

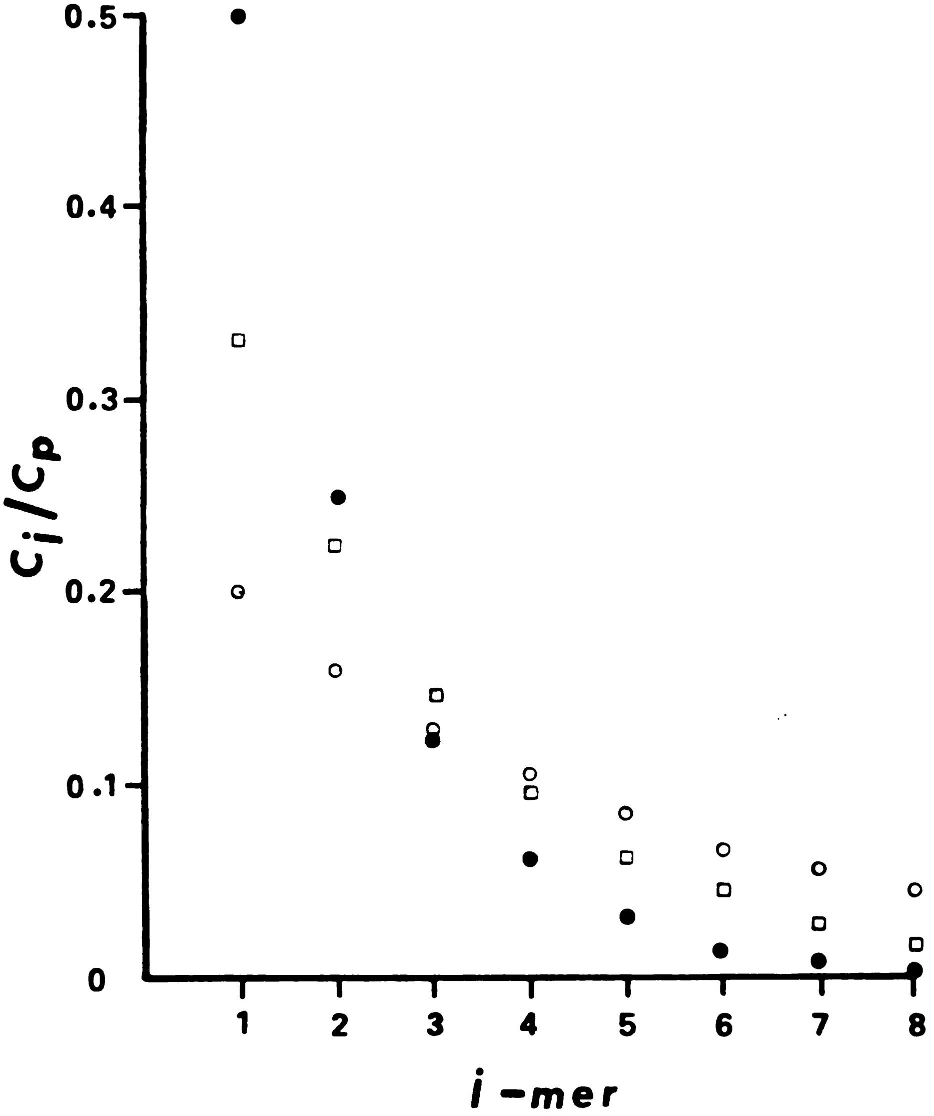

Figure 2-2. Distribution of i-mer for open associating systems. (●) $M_a/M_1=2$; (□) $M_a/M_1=3$; (○) $M_a/M_1=5$.

where

$$\zeta \equiv \sqrt{1 + 8P} \qquad (2\text{-}10)$$

Equation (4) in Part One for the open association model and Equation (2-6) for the dimerization model are compared in Figure 2-1. Ψ_1 of the open association is a more rapidly decreasing function of P, especially at higher concentrations. This can be explained intuitively by the argument that the open association model allows multimers larger than dimers to exist in the solution. The difference is smaller at low concentrations. In fact, the two plots in Figure 2-1 have the same initial slope $-K/M_1^2$. However, the PEG/benzene data in this work can be described satisfactory only by the open association model.

CHAPTER III

EXPERIMENTAL METHOD

A. Polymer Sample

Polyethylene glycol (PEG) in benzene is chosen for studying association in this work because it has been shown [B-15, B-16, B-34] that the hydroxyl endgroups can form hydrogen bonds either with other hydroxyl endgroups or with the ether groups in this system.

Monodisperse PEG samples were purchased from Polymer Laboratories Inc., Massachusetts. The samples were used without further purification. The polydispersity of the samples are listed in Table 3-1.

Table 3-1. Polydispersity of the PEG samples.

M	M_w/M_n
440	<1.09
960	<1.06
4250	<1.03
12600	<1.04

B. Osmometry Data

When the free energy of a solution has been diminished by an addition of solute, it is possible to compensate for this reduction by applying an external pressure to the solution. For example, when solvent molecules diffuse through a semi-permeable membrane from a dilute solution into a more concentrated one through the process of osmosis, it is possible to prevent the diffusion by applying an external pressure (called the osmotic pressure) .

Osmotic pressures are frequently used to determine the molecular weight of a polymer and to study the thermodynamics of polymer solutions (such as second virial coefficient, Flory-Huggins interaction parameter, and activity coefficient). A plot of reduced osmotic pressure versus concentration for a dilute polymer solution often yields a straight line, and the number-average molecular weight of the polymer can be determined by extrapolating the data to zero concentration [B-7, B-24, B-25]. However, if a straight line is not obtained, it is necessary to repeat the measurements with several different solvents to prevent faulty extrapolations.

The membrane osmometer [B-43, B-52] is commonly used for measuring the osmotic pressures of polymer solutions. The best type is the electrical and automatically recording dynamic osmometer which usually allows equilibrium to be reached within 30 minutes. However, its usefulness is limited to molecular weights range from 5 x 10^3 to 5 x 10^5 [B-7, B-43, B-52]. The upper limit is determined by the smallest osmotic pressure that can be read, and the lower limit is determined by the permeability of the membrane. In addition, it is often difficult to find a suitable membrane for a particular polymer-solvent pair. The membrane must not be dissolved by the solvent. If the pores of the membrane are too small, the measurements take a long time. On the other hand, if they are too large, polymer molecules may leak through the membrane. Such a membrane is not always available.

For molecular weights under 2 x 10^4, highly sensitive vapor pressure osmometers should be used [B-43, B-52]. Vapor pressure osmometry is an indirect method for measuring molecular weights and osmotic pressures, and a standard is required for calibration. This kind of osmometer offers the advantages that it requires no membrane, needs only a small amount of sample, and is very easy to operate.

The vapor pressure osmometry data of Elias [B-15, B-19] for PEG in benzene at 25°C were used in this work.

C. Diffusivity data

Diffusion coefficients in this work were measured using a Mach-Zehnder interferometer [B-5, B-10]. The description of this apparatus and its operation have been given in many places [B-5, B-27, B-35, B-39] and are not repeated in detail here. A complete description can be found in the dissertation of Bidlack [B-5]. Although the Mach-Zehnder interfermometer was developed a few decades ago, it remains one of the most accurate methods for measuring the concentration dependence of diffusion in solution [B-11].

The interferometry technique involves carefully bringing a more concentrated solution into contact with a less concentrated solution to form a sharp interface in an optical cell where free diffusion is allowed to take place. The optical cell is immersed in a well-controlled temperature bath. The diffusion rate can be followed by measuring the refractive index in the cell as a function of time and position. If refractive index is assumed linear with concentration over small concentration ranges, the diffusion coefficient can be calculated from photographs of this fringe pattern at several times during the diffusion process. The concentration for the measurement is taken to be the arithmetic average of the original solution concentrations.

The interferometer was checked by comparing the diffusion coefficients of five aqueous sucrose solutions at 25 °C with those reported by Gosting and Morris [B-22]. The data of Gosting and Morris have been confirmed by several investigators [B-2, B-12] and can be fitted by the method of least squares to the empirical relationship

$$D = 5.226 (1 - 0.01480 c) \times 10^{-6} \pm 0.002 \qquad (3-1)$$

where c is the sucrose concentration in grams per 100 cm^3 of a water solution diffusing into pure water. A summary of the comparison is presented in Table 3-2. The standard deviation is found to be less that 1%.

Table 3-2. Comparision of the diffusivity data determined in this work with the data of Gosting and Morris.

	$D \times 10^6$, cm^2/sec		% deviation
c, grams/100 cm^3	This work	Equation (3-1)	
0.4	5.220	5.195	+0.48
0.6	5.201	5.180	+0.41
0.8	5.191	5.164	+0.52
1.0	5.158	5.149	+0.17
1.2	5.108	5.133	-0.49

The experimental procedure described by Bidlack [B-5] was used in this work. The solutions were prepared and agitated gently for about three hours before using. The concentration differences between the two solutions were chosen to be 0.40 g/dl for all runs. The temperature bath was maintained at 25.0 ± 0.1 °C. Each experiment took from 30 minutes to an hour for completion, depending on the molecular weight. Six exposures were usually taken for each run.

Because of the small refractive index difference between the PEG/benzene solutions, the number of fringes, J (see reference [B-5]), was usually less than 10. It was vital to measure the value of J (i.e., the total refractive difference between the two solutions) with great accuracy, for a slight error could change the result significantly. Each exposure provides a value of J. Since there were six exposures per run, six values of J were obtained and the average was used to calculate the diffusion coefficient. If the difference between the largest and the smallest values of J exceeded 0.3, the run was discarded. The accuracy of the diffusion coefficients reported in this work were estimated to be within 4%. A sample calculation is presented in Appendix A.

CHAPTER IV

THERMODYNAMICS OF ASSOCIATING POLYMER SOLUTIONS

A. Theoretical Background

The behavior of polymer solutions deviates greatly from Raoult's law except at extreme dilutions. Excess thermodynamic properties are large even for systems of negligible heat of mixing. This is due to the large entropy effect for mixing giant long-chain polymer molecules with small solvent molecules. Below are some theories used frequently to describe the thermodynamics for nonassociating polymer solutions. In this work, an attempt is made to extend the applications of these theories to associating systems by replacing the unimer molecular weight with the apparent molecular weight.

1. Flory-Huggins Theory

The Flory-Huggins theory [B-21] has been used extensively due to its simplicity. This theory expresses the change in free energy of mixing as

$$\frac{\Delta G_m}{R\,T} = n_s \ln\phi_s + n_p \ln\phi_p + \phi_s\phi_p(n_s + mn_s)\chi \qquad (4\text{-}1)$$

where the subscript s designates the solvent and the subscript p the polymer. ϕ and n are the volume fraction and number of moles, respectively. m is the ratio of molar volumes of polymer to solvent.

χ is called the Flory-Huggins interaction parameter. It is a dimensionless quantity and a function of the interaction energy characteristic of a given solute-solvent pair. It consists of both entropic and enthalpic contributions and can be expressed empirically by [B-41]

$$\chi = \chi' + \frac{V_s}{RT} (\delta_s - \delta_p)^2 \tag{4-2}$$

where χ' is the entropy parameter with value between 0.3 and 0.4. δ_s and δ_p are "solubility parameters" of the solvent and the polymer, respectively. V_s is the molar volume of the solvent and R is the gas constant.

The thermodynamic quality (good solvent versus bad solvent) can be evaluated in terms of χ. Note that the free energy must be negative for the polymer to dissolve in the solvent. Since the first two terms in Equation (4-1) are always negative, the solubility of the polymer is determined solely by the magnitude of χ. It can be said that the smaller the value for χ, the more negative the value of ΔG_m, and the better the solvent for the polymer. A good solvent is defined as one in which the interaction between polymer and solvent is stronger than that between polymer and polymer.

2. Two-Parameter Theory

The two-parameter theory [B-50, B-57] is a group of theories which express the properties (such as second virial coefficients and viscosities) of dilute polymer solutions in terms of two basic parameters.

Since polymer molecules in solution are constantly coiling and uncoiling owing to thermal fluctuations, it is possible to characterize their dimensions only by averages. One of these averages is the mean-square end-to-end distance of an unperturbed chain, $\langle R^2 \rangle_o$. The word "unperturbed" implies that the polymer chain is completely free of outside influences. Unperturbed dimensions are affected only by the so-called "short-range interferences" due to fixed bond angles and hinderances to rotation. The parameter [B-21, B-52]

$$A \equiv \left\{ \frac{\langle R^2 \rangle_o}{M} \right\}^{\frac{1}{2}} \tag{4-3}$$

is often used to characterize the unperturbed state because this quantity is almost independent of molecular weight for sufficiently long chains, and its values are readily available for a large number of polymer-solvent pairs [B-9].

For a given polymer, A depends on temperature and solvent characteristics. However, the solvent effect is usually insignificant, at least for nonpolar polymers [B-9].

There are also the so-called "long-range interferences" or "excluded volume effects". They arise because two segments cannot occupy the same space at the same time. The mean-square radius of gyration for a real linear macromolecule in an infinitely dilute solution is generally expressed as [B-4, B-57]

$$\langle S^2 \rangle = \alpha_s \langle S^2 \rangle_o \tag{4-4}$$

The expansion factor α_s measures the extent to which the excluded volume perturbs the polymer molecule from its unperturbed state. In contrast to A, information on α_s is generally not available and it depends on temperature, polymer molecular weight, and solvent characteristics.

The excluded volume effects can be eliminated by a judicious choice of solvent and temperature. The polymer chain contracts in poor solvents because the polymer segments prefer to associate with other polymer segments rather than with solvent molecules. When the contraction due to poor solvent balances the expansion due to the excluded volume, the net excluded volume is zero and the solution is in the unperturbed or the theta state.

A common application of the two-parameter scheme [B-50, B-57] is to express the expansion factor α_s as

$$\alpha_s = \alpha_s\ (A,\ B,\ M) \tag{4-5}$$

Yamakawa-Tanaka [B-55] suggest the expression:

$$\alpha_s^2 = 0.541 + 0.459\ (1 + 6.04\ z)^{0.46} \tag{4-6}$$

where

$$z = \left(\frac{3}{2\ \pi}\right)^{3/2} \frac{M^{\frac{1}{2}}\ B}{A^3} \tag{4-7}$$

The parameter A represents the short-range interferences, and the parameter B the long-range interferences. As mentioned earlier, A can be obtained rather easily.

B is a function of temperature and solvent. The preferred method for calculating B involves light-scattering measurements to determine α_s at several polymer molecular weights [B-57]. The quantity z can then be determined for each value of M from Equation (4-6), and by Equation (4-7) B can be estimated from the slope of z versus $M^{1/2}$ plot. The shortcoming of this approach is that very limited light-scattering measurements are available in the literature.

An alternative for estimating B is to use the intrinsic viscosity relation [B-21, B-57]

$$[\eta] = K_v M^{\beta} \tag{4-8}$$

Values of K_v and β have been tabulated for many polymer-solvent pairs [B-9]. The parameter B can be estimated from the equation [B-50, B-57]

$$B = \frac{K_V M^{\beta-\frac{1}{2}} - 1.05\Phi A^3}{0.2787\Phi M^{\frac{1}{2}}} \tag{4-9}$$

which can be used when $BM^{1/2}/A^3 < 5.06$. Kurata et al. [B-32, B-33] recommend $\Phi = 2.7 \times 10^{23}$ for well-fractioned polymer ($M_w/M_n < 1.1$) and $\Phi = 2.5 \times 10^{23}$ for ordinary fractioned polymers ($M_w/M_n > 1.1$).

Although the two-parameter theory provides satisfactory predictions for the properties of flexible polymer chains in dilute solution, it breaks down for stiff chains and for the region far away from the theta state ($|z| < 0.15$) [B-57].

3. Second Virial Coefficient

As a general rule, polymer solutions seldom behave ideally except at infinite dilution. A convenient way to describe the nonideal behavior of a polymer solution is to express the chemical potential of the solvent, μ_s, in terms of the power series [B-21, B-57]:

$$\mu_s - \mu_s^0 = R\ T\ V_s \rho (1/M + A_2 \rho + A_3 \rho^2 + \dots) \tag{4-10}$$

where V_s is the molar volume of the solvent. A_2 and A_3 are the osmotic second and third virial coefficients, respectively. The virial coefficients represent the binary and higher-order interactions of polymer molecules due to excluded volume effects. In dilute solutions, it is sufficient to consider only the second virial coefficient because the influence of the third and higher order virial coefficients are usually relatively small.

The second virial coefficient for a dilute polymer solution has several significant meanings. It is directly related to the chemical potential of the solvent, the excluded volume, and the Flory-Huggins interaction parameter. It may also be used to measure the goodness of a solvent for a particular polymer--good solvents are commonly defined as those having positive A_2.

The relationship between A_2 and the excluded volume depends on the geometry of the polymer molecules. If the polymer molecules behave like rigid spheres, the excluded volume per sphere, u, (see Figure 4-1) is [B-24]

$$u = 4\ (\text{volume of sphere}) \tag{4-11}$$

and it can be shown that the second virial coefficient can be related to u by

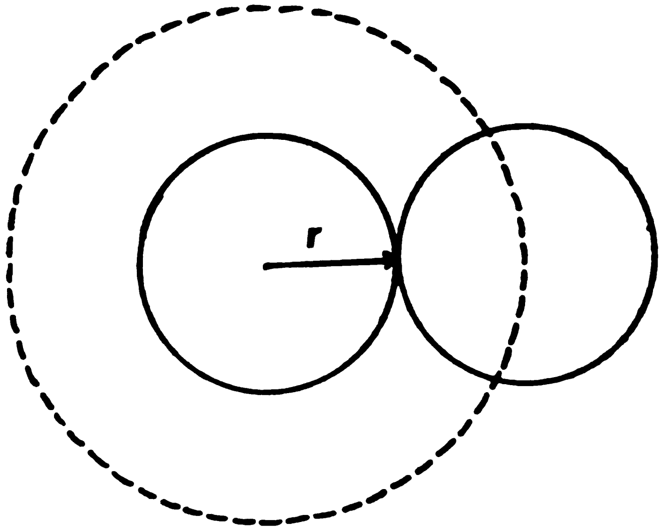

Figure 4-1. The excluded volume (dotted volume) for two spheres in contact.

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$$A_2 = N_a\, u / 2\, M^2 \tag{4-12}$$

Since the volume of a spherical molecule is proportional to the molecular weight M, the second virial coefficient for rigid sphere molecules is inversely proportional to M. For rigid rod molecules, the second virial coefficient is independent of the molecular weight [B-57].

In general, the second virial coefficient can also be correlated with the molecular weight by the relation [B-9]

$$A_2 = K'\, M^{-\alpha} \tag{4-13}$$

where K' and α are empirical constants which depend on the polymer, solvent and temperature. As mentioned earlier, $\alpha=1$ for rigid spheres and $\alpha=0$ for rigid rod molecules. The relation is usually valid only within limited molecular weight range, and for most systems the values of α are found to be less than 0.5 [B-9].

Since the osmotic pressure can be obtained from the Flory-Huggins theory [B-21]

$$\frac{\pi}{\rho R T} = \frac{1}{M} + (\tfrac{1}{2} - \chi)\, \frac{V_p^2}{V_s\, M^2}\, \rho + \ldots \tag{4-14}$$

it can been shown easily that the second virial coefficient and χ are related by

$$A_2 = (\tfrac{1}{2} - \chi)\, \frac{V_p^2}{V_s\, M^2} \tag{4-15}$$

When $\chi = 1/2$, $A_2 = 0$, the excluded volume vanishes, and the solution is said to be under theta conditions. This situation arises because of the apparent cancellation between the enthalpy of mixing and the excess entropy of mixing.

B. Expression for Osmotic Pressure for Associating Polymer Solutions

In Part One, an expression for the concentration dependence of osmotic pressure has been derived:

$$\Pi \equiv \frac{M_1 \pi^*}{\rho R T}$$

$$= \Psi_1 + A_2^* M_1 \rho + \ldots \qquad (4\text{-}16)$$

where A_2^* is assumed to be independent of concentration for each molecular weight. In this section, Equation (4-16) is extended to include the concentration dependence of A_2^*, and the osmotic pressure is expressed in terms of the unimer molecular weight, the mass concentration, the association constant K, and the parameter α in Equation (4-13).

First, an approximation for A_2^* is made. A_2^* is a complicated term because it includes the interactions between all multimers (such as unimer-unimer, unimer-dimer,

dimer-dimer, etc.). Recently Tanaka and Solc have shown that A_2^* can be approximated by [B-45]

$$A_2^* \cong A_{2,n} \qquad (4\text{-}17)$$

where $A_{2,n}$ is the second virial coefficient of a monodisperse polymer with molecular weight equal to the number-average molecular weight of the multimer mixture. (In Tanaka and Solc's paper, open association is identified as a heterogeneous polymer solution having a Schultz-Zimm distribution and a polydispersity less than 2.) For excluded volume parameter $z < 5$, this approximation is accurate within 5%. Since the sizes of the multimers vary with concentration, $A_{2,n}$ also varies with concentration.

Next, A_2^* is expressed in terms of the second virial coefficient of unimer, A_{21}. The motivation is that A_{21} can be calculated easily by the two-parameter theory. If equation (4-13) can be applied to the multimers such that

$$A_{2i} = K' M_i^{-\alpha} \qquad (4\text{-}18)$$

where A_{2i} is the second virial coefficient of i-mer, then

$$A_{21} = K' M_1^{-\alpha} \qquad (4\text{-}19)$$

and

$$A_{2,n} = K' M_a^{-\alpha} \qquad (4\text{-}20)$$

Substituting Equations (4-19) and (4-20) into Equation (4-17), A_2^* can be expressed as

$$A_2^* = A_{21} (M_1/M_a)^{-\alpha}$$

$$= A_{21} \Psi_1^{-\alpha} \qquad (4\text{-}21)$$

where Ψ_1 has been defined previously (Equation (4) in Part One) as M_1/M_a.

Substituting Equation (4-21) into Equation (4-16), the osmotic pressure can be expressed as

$$\Pi = \Psi_1 + A_{21} \Psi_1^{-\alpha} M_1 \rho + \ldots \qquad (4\text{-}22)$$

The observed second virial cofficient obtained from differentiating this equation with respect to ρ and evaluating the result at $\rho=0$ is

$$(A_2^*)_{obs} = A_{21} - K / M_1^2 \qquad (4\text{-}23)$$

which is the same as Equation (16) in Part One.

Equation (4-18) is valid for positive A_2 only. Because A_2 may become negative as molecular weight decreases, application of Equation (4-22) is restricted to polymer molecules of ordinary size (with molecular weight higher than 10^4).

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C. Presentation of Osmometry Data and Discussions

1. Estimation of K

According to Equation (4-23), if the dependence of A_{21} on M_1 is relatively weak compared to that of K/M_1^2, a plot of $(A_2^*)_{obs}$ versus $1/M_1^2$ should yield a straight line with slope equal to -K. The values for $(A_2^*)_{obs}$ can be obtained from the initial slope of $\pi^*/\rho RT$ versus ρ.

The osmometry data of Elias [B-16, B-19] for PEG in benzene are used here to test this equation. Since the data can be well fitted by a straight line (see Figure 4-2), the slope is a good initial guess for K. The final value of K calculated based on the association model and the least squares method is 11000 ± 300 cc/mole.

Association of PEG in benzene has also been studied by Afifi-Effat and Hay [B-1]. Their association model predicted that

$$(A_2^*)_{obs} = A_{21} - K / M_1 \qquad (4\text{-}24)$$

and they claimed that their data were in good agreement with this prediction. However, this author found a lack of consistency between their raw data, calculations, and results. The data of Elias do not agree with Equation (4-24). (A plot of $(A_2^*)_{obs}$ versus $1/M_1$ is not linear.)

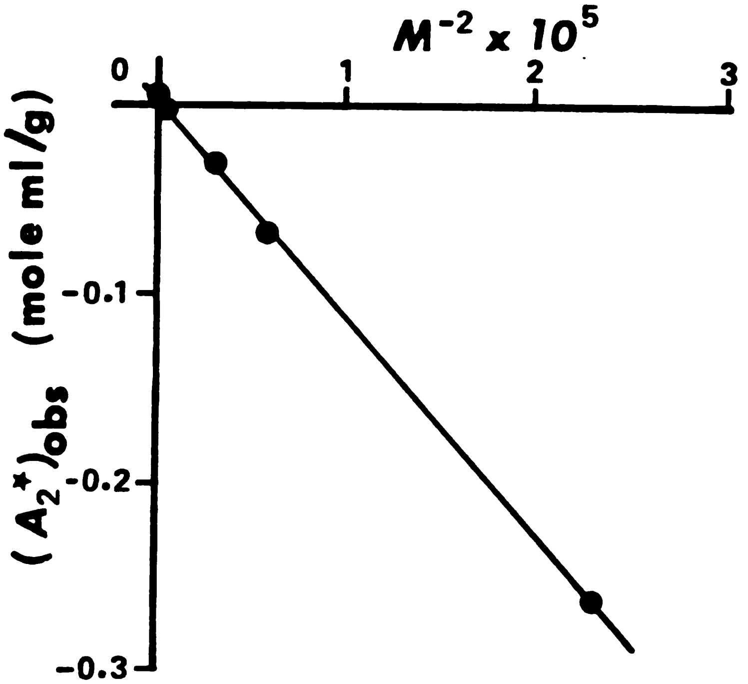


Figure 4-2. $(A_2^*)_{obs}$ versus $1/M_1$. Experimental data taken from Elias et al. [B-16, B-19].

2. Estimation of A_2^*

The two-parameter theories can be used to estimate the second virial coefficient for linear, flexible chain polymers [B-50, B-57]:

$$A_2 = \frac{N_a\, B\, h_o(\bar{z})}{2} \tag{4-25}$$

where

$$\bar{z} = \frac{z}{{\alpha_s}^3} \tag{4-26}$$

$$h_o\,(\bar{z}) = \frac{0.547\,\{1 - (1 + 3.903\bar{z})\}^{-0.4683}}{\bar{z}} \tag{4-27}$$

Thus the second virial coefficient A_2 of PEG in benzene at 25 °C can be easily estimated if the parameters A and B are known. The parameter A, which represents the short-range interferences, is given by [B-9]

$$A = \left\{\frac{\langle R^2\rangle_o}{M}\right\}^{\frac{1}{2}} = 7.9 \times 10^{-9}\ \text{cm} \tag{4-28}$$

The parameter B, which represents the long-range interferences, is estimated indirectly from the empirical

Mark-Houwink intrinsic viscosity relationship (see Equations (4-8) and (4-9)):

$$[\eta] = K_v \ M^{\beta} = 0.063 \ M^{0.64} \qquad (4\text{-}29)$$

where $[\eta]$ is the intrinsic viscosity in ml/g. The values of K_v and β in Equation (4-29) are obtained from curve fitting the raw data of Rossi and Cuniberti [B-42] using the method of least squares. It should be pointed out that Rossi and Cuniberti fitted their data with different values of K_v and β:

$$[\eta] = 0.00129 \ M^{0.5} \qquad (4\text{-}30)$$

because they were preoccupied by the idea that α should always be 0.5. However, their raw data clearly agree only with Equation (4-29), and the use of Equation (4-30) is incorrect.

Figure 4-3 shows the second virial coefficient as a function of molecular weight for PEG in benzene at 25 ^{o}C, predicted by the two-parameter theory. The value of A_2 increases very rapidly with molecular weight before it reaches a maximum. (When $M<297$, $B<0$ and the theory predicts negative values for A_2.) For higher molecular weights, A_2 decreases (not so rapidly) with increasing molecular weight. In short, A_2 can be positive or negative, increasing or decreasing functions of molecular weight, depending on the situation.

Figure

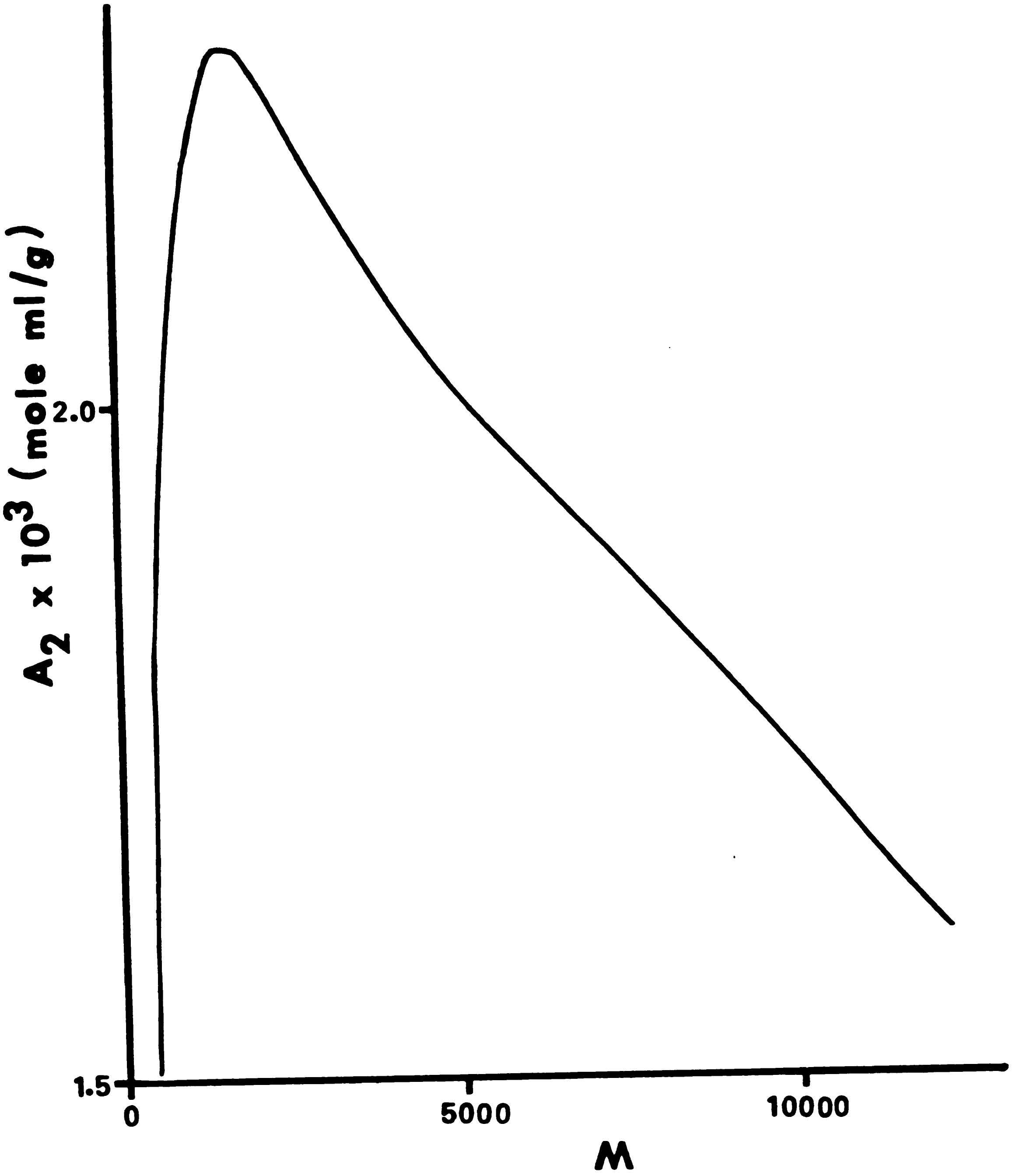


Figure 4-3. Molecular weight dependence of the second virial coefficient for PEG in benzene, predicted by the two parameter theory (Equation (4-25)).

The two-parameter theory expresses A_2 in such a complicated function that the derivation of a diffusion coefficient equation using this function is extremely difficult. An alternative is to assume a simplier relation such as $A_2 = K' M^{-\alpha}$. In fact many polymer-solvent pairs have been found to obey this relation [B-4, B-9]. Expressions for the concentration dependence of osmotic pressure and diffusion coefficient based on this relation has been derived in Section B of this chapter.

However, the relation $A_2 = K' M^{-\alpha}$ is valid only for positive A_2. It cannot be used to describe the data of Elias because some of these data (M_1=208, M_1=409) must take negative A_2 if they are to fit the open association model. Of course, a more sophisticated relation may correct this suitation, but it also leads to expressions that are very difficult to use in diffusion theory.

One solution to this problem is to assume an A_2^* independent of concentration for each polymer sample when calculating (see Equation (15) in Part One). In other words, for five samples (as is the case for Elias' data) five A_2^*'s are used, and each is an average over the concentration. The values for A_2^* obtained using this assumption are plotted as a function of molecular weight in Figure 4-4. This plot is in qualitative agreement with the

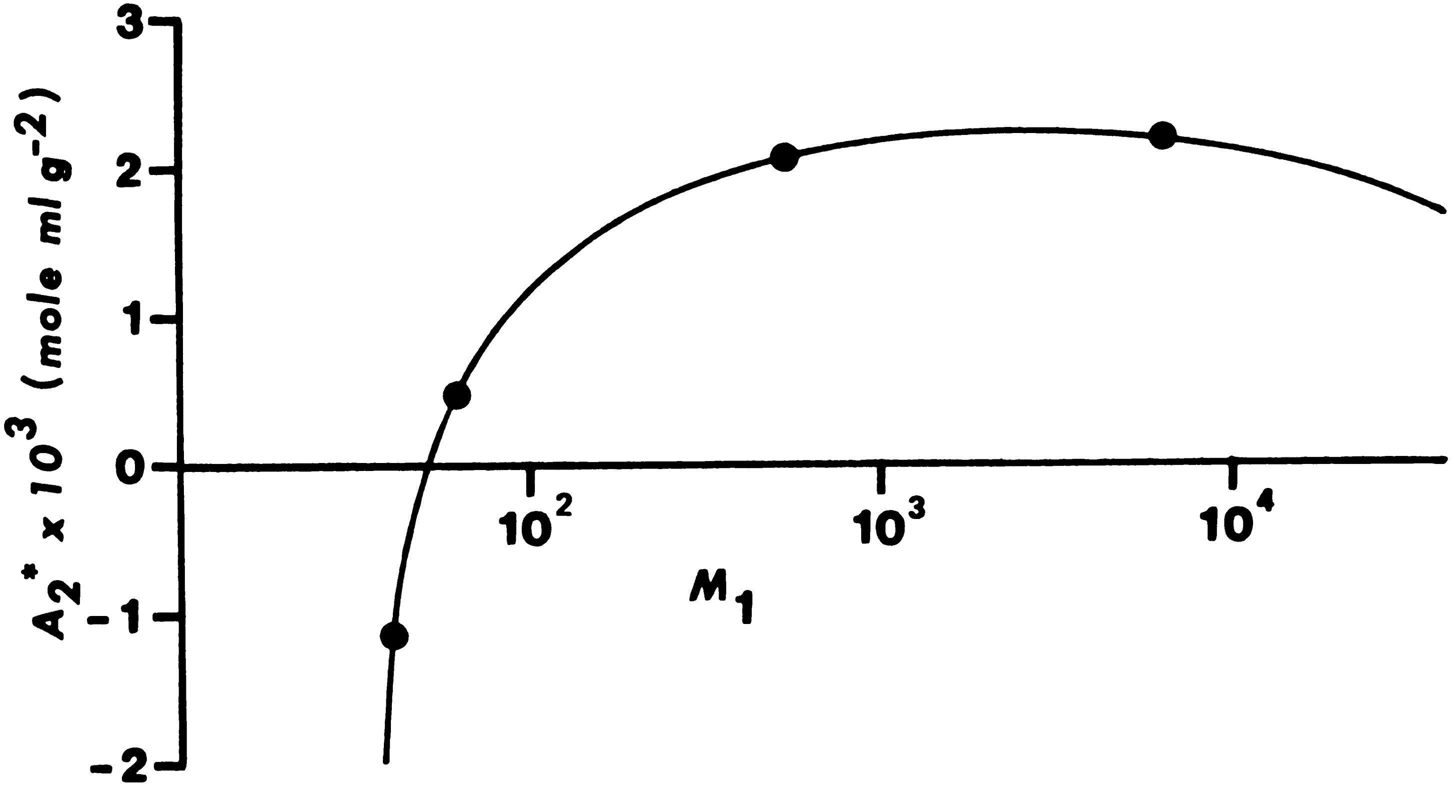


Figure 4-4. Values of A_2^* (from Table I in Part One) versus M_1.

predictions from the two-parameter theory (compare with Figure 4-3).

For high molecular weights, this assumption is valid because the second virial coefficient is a weak function of molecular weight [B-4, B-9, B-21, B-32] and concentration. For low molecular weights, the justification for this assumption is as follows. According to Equation (15) in Part One, Π consists of two terms: the association term Ψ_1 and the virial term $A_2^*M_1\rho$. If the virial term is sufficiently small, the error introduced by this assumption in calculating Π is negligible. Figure 4-5 shows the magnitudes of these two terms plotted against concentration for two molecular weights. It is seen that the virial term for the low molecular weight sample (M_1=594) is very small. Consequently, this assumption can also be used for low molecular weights.

3. Other Discussion

As shown in Figure 4-5, the association term is a decreasing function of ρ, but the virial term is an increasing function of ρ. For the low molecular weight sample (M_1=594), the association term dominates; for the high molecular weight sample (M_1=6000), the virial term dominates. It is interesting that the effects of these two terms sometimes balance each other, as for the sample

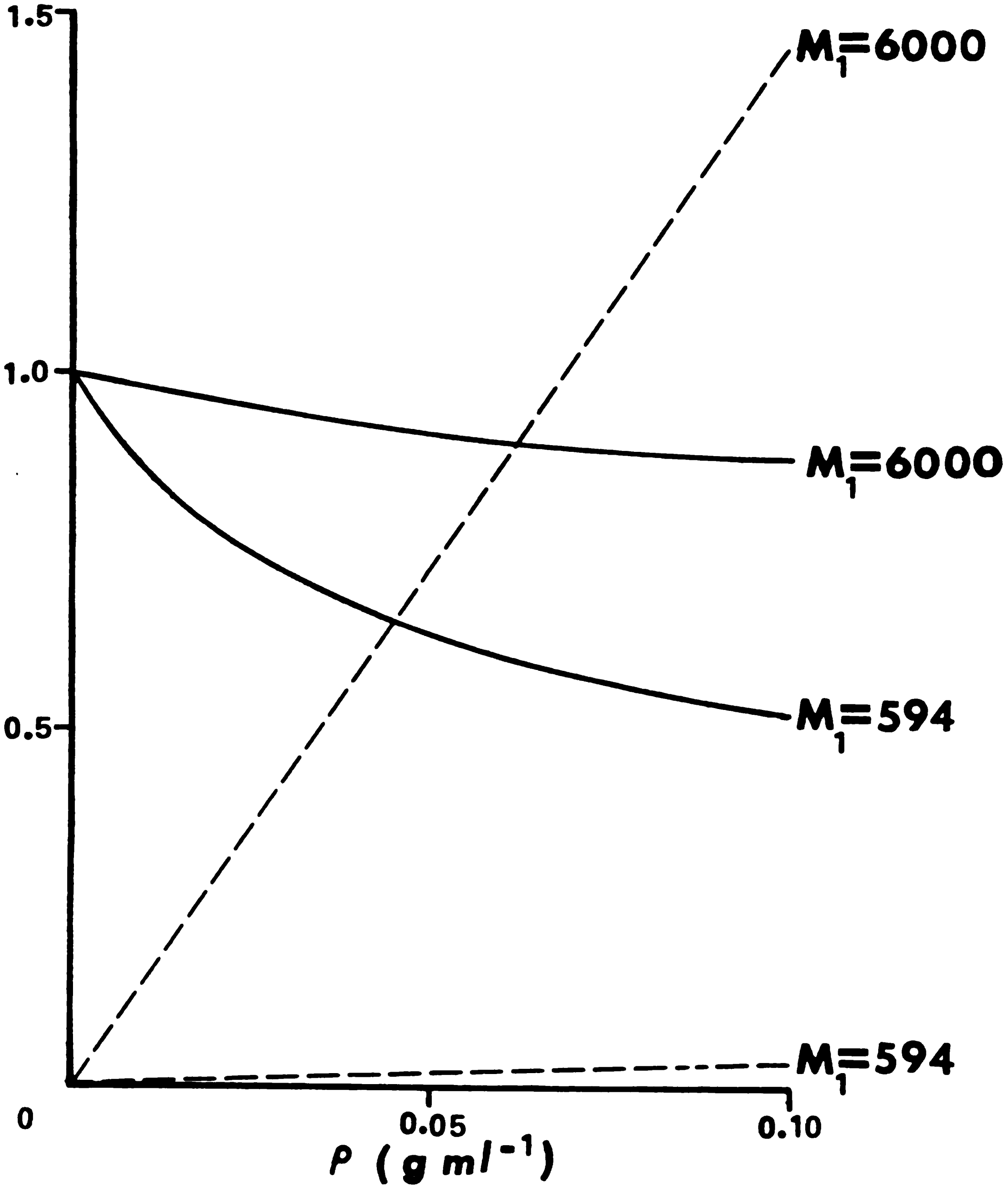


Figure 4-5. Comparison of the association term (———) with the virial term (-----) in Equation (15), in Part One, for PEG in benzene at 25 °C.

(M_1=1518). Π for this sample (see Figure 1 in Part One) is almost unity regardless of concentration, and thus it behaves like one under theta conditions (see Chapter II). When both terms are large, the model predicts that the association term dominates at low concentrations while the virial term dominates at higher concentrations. In this case, a plot of Π versus ρ should first pass through a minimium and then increase with ρ. This behavior has already been observed in some systems [B-18, B-35].

Although the sample (M_1=6000) displays a linear behavior and can be satisfactorily described by the nonassociating model, it is incorrect to assume that association does not occur at higher molecular weights. In fact, Elias has shown that the association constant is independent of molecular weight [B-19].

CHAPTER V

DIFFUSION IN ASSOCIATING POLYMER SOLUTIONS

A. Theoretical Background

Diffusion is movement of a chemical species from a region of higher concentration to a region of lower concentration. The flow of solute molecules per unit time across a unit area perpendicular to the direction of flow (x axis), J, is given by Fick's law

$$J = - D\frac{\partial c}{\partial x} \qquad (5\text{-}1)$$

where D is known as the diffusion coefficient.

The diffusion coefficients of many polymer solutions depend strongly on the nature of the solvent and polymer concentration. Most of the studies in this area indicate that for dilute polymer solutions in good solvents, the value of D generally increases with polymer concentration. On the other hand, the values of D for films or solids in the region near the undiluted polymer generallly increase sharply with increasing diluent concentration. Therefore $D(\rho)$ in good solvents can be expected to exhibit a maximum at an intermediate concentration from pure solvent to pure polymer.

In addition to solvent and polymer concentration, the diffusion coefficient may also be affected by molecular association. The larger associated complexes (dimers, trimers, etc.) diffuse much slower than the unimers, leading to lower diffusion coefficients.

The concentration dependence of diffusion coefficient in dilute polymer solutions is often expressed as [B-50, B-57]

$$D = D_o \left(1 + k_d \rho + \ldots \right) \tag{5-2}$$

Accordingly, predicting the value of D requires the knowledge of D_o and k_d. At the present time, D_o can best be predicted by the Kirkwood-Riseman theory, and k_d by the Pyun-Fixman theory.

1. Kirkwood-Riseman Theory

The Kirkwood-Riseman theory [B-29, B-30, B-57] provides a simple method for predicting the diffusion coefficient for linear, flexible polymer chains at infinite dilution under theta conditions. Infinite dilution implies that the polymer molecules are widely dispersed in the solvent and there are no interactions between individual polymer chains.

This theory is applicable only under theta conditions because the excluded volume effects are not included in the derivation.

Its derivation is based on the assumption (the nonfree draining limit) that there exists a very large hydrodynamic interaction between polymer segments, and the polymer chains behave like rigid molecules. The Kirkwood-Riseman theory is expressed as

$$(D_o)_\theta = \frac{0.196\ k\ T}{\eta_s\ A\ M^{\frac{1}{2}}} \qquad (5\text{-}3)$$

where k is the Boltzman constant and η_s is the viscosity of the solvent. Since A and η_s are usually available, the determination of $(D_o)_\theta$ for many polymer-solvent pairs are relatively simple. For solutions under nontheta conditions, Duda et al. have suggested the modified form [B-48, B-50]

$$D_o = \frac{(D_o)_\theta}{\alpha_s} \qquad (5\text{-}4)$$

where D_o is the diffusion coefficient at infinite dilution under nontheta conditions, and αs is the expansion factor defined previously. Since $\alpha s \geq 1$ except for very poor solvents,

$$(D_o)_\theta \geq D_o \qquad (5\text{-}5)$$

and thus the Kirkwood-Riseman theory provides an upper bound for the diffusion coefficient at infinite dilution.

Duda et. al. [B-51] compared the predictions of this theory with the experimental values of $(D_o)_\theta$ for polystyrene in cyclohexane under theta conditions. The predictions were found to be slightly higher than the experimental values. The average ratio of D_o(exptl) to Do(theory) was 0.86.

2. Modified Pyun-Fixman Theory

The behavior of dilute polymer solutions changes significantly with polymer concentration. As concentration increases, the polymer molecules interact hydrodynamically with each other even though they may not overlap or entangle.

The concentration dependence of diffusion coefficient, k_d, can be expressed as [B-49]

$$k_d = 2 A_2 M - k_s - 2 V_{po} \tag{5-6}$$

where A_2 is the thermodynamic second virial coefficient, and V_{po} is the partial specific volume of the polymer at infinite dilution. The quantity k_s is defined by the series expansion [B-49]

$$f = f_o (1 + k_s \rho + \dots) \tag{5-7}$$

and f is the friction coefficient defined by the relation

$$\text{force on a polymer molecule} = f\ (u_p - u_s) \qquad (5\text{-}8)$$

where u_s and u_p are the velocities of solvent and polymer, respectively, with respect to a convenient reference frame.

According to Equation (5-6), the value of k_d depends on the thermodynamic, hydrodynamic and volumetric effects. The thermodynamic effect, A_2, has already been discussed in Chapter IV; the hydrodynamic effect, k_s, can be estimated by the Pyun-Fixman theory; and the volumetric effect, V_{po}, can be measured from density experiments. The effect of V_{po} is usually relatively small, and can be ignored if k_d is less than 20 cm^3/g.

The Pyun-Fixman theory [B-38, B-54, B-57] is based on a spherical model in which the spheres are composed of both polymer and untrapped solvent. It can be expressed as

$$ks = \left\{2.23\ 6^{\frac{1}{2}}\ \pi^{\frac{5}{2}}\ N_a M\ A^3/512\right\} - V_{po} \qquad \text{(version I)} \qquad (5\text{-}9)$$

or

$$ks = \left\{2.23\ 6^{\frac{1}{2}}\ \pi^{\frac{5}{2}} N_a M\ A^3/512\,\lambda^3\right\} - V_{po} \qquad \text{(version II)} \qquad (5\text{-}10)$$

under theta conditions. Equation (5-9) is called version I, and Equation (5-10) version II, of the Pyun-Fixman theory

[B-51]. They are related by the parameter λ which is defined as

$$\lambda \equiv (D_o)_{\theta,\mathrm{exptl}} / (D_o)_{\theta,\mathrm{theory}} \tag{5-11}$$

To extend its application for nontheta conditions, Duda et al. [B-53] have suggested the following expressions

$$k_s = [7.16 - K(A_o^*)]\,\frac{4\pi a_o^3 N_a}{3M} - V_{po} \tag{5-12}$$

$$a_o = \frac{6^{\frac{1}{2}}\pi^{\frac{1}{2}} A M^{\frac{1}{2}} \alpha_s}{16} \tag{5-13}$$

$$A_o^* = \frac{4096\ z}{72\ \alpha_s^3 \pi} \tag{5-14}$$

$$K(A_o^*) = 24\int_0^1 \left\{ \frac{2\ \ln[1 + x + (2x + x^2)^{\frac{1}{2}}]}{(2x + x^2)^{\frac{1}{2}}} - 1 \right\} x^2 \exp[-A_o^*(1 - x)^2(2 + x)]\,dx \tag{5-15}$$

which are collectively called the modified Pyun-Fixman theory. Thus if A, B and V_{po} are known for a particular polymer-solvent pair, k_s can be calculated in a straight-forward manner. When z=0 and α_s=1 (i.e., under theta conditions), Equations (5-12) through (5-15) reduce to

Equation (5-9). However, it remains for future work to test the modified Pyun-Fixman theory with experimental data.

B. Expression for Diffusion Coefficient for Associating Polymer Solutions

In Part One, an expression for the concentration dependence of diffusion coefficient for associating systems has been derived, assuming that A_2^* is independent of concentration for each molecular weight. Following the same procedure as described in Part One, the diffusion coefficient D^* based on Equation (4-16) can be expressed as

$$D^* = \left\{1 - (k_s + 2V_{po}) \frac{M_1}{K} P\right\} \left\{ 2A_{21} \frac{M_1^2}{K} \left(\frac{2}{1+\xi}\right)^{\alpha-1} \left(1 - \frac{\alpha P}{\xi(1+\xi)}\right) P - \frac{2P}{\xi(1+\xi)} + 1 \right\} + \ldots \qquad (5\text{-}16)$$

where

$$\xi = \sqrt{1 + 4P} \qquad (5\text{-}17)$$

as defined previously. In deriving this equation, the parameters k_s, f and V_p were expanded in terms of a power series with concentration, and only the first-order terms are retained. When $\alpha = 0$ (i.e., A_2^* is independent of molecular weight), this expression reduces to Equation (23) in Part One. Note that Equation (5-16) is considerably more complicated compared with Equation (23). In addition, the parameter α must be estimated.

C. Presentation of PEG Diffusivity Data and Discussions

1. Estimation of D_o

The Stoke-Einstein theory [B-6, B-40]

$$D = k\,T / 6\pi\eta r \qquad (5\text{-}18)$$

is often used to estimate the diffusion coefficient of liquids. k is the Boltzmann's constant, η the solvent viscosity, and r the solute radius. This theory is valid only for large, spherical molecules diffusing in dilute solutions. Moreover its direct application is not always possible because the solute radius r is often not available. However, many authors have used the form $D\eta/T = f(\text{solute size})$ as a starting point in developing empirical correlations [B-40].

Polymer molecules in solution, in general, do not behave like large spherical molecules. They are best imagined to be like necklaces consisting of spherical beads connected by strings that have no resistance to flow. Consequently, the Stoke-Einstein equation fails to accurately predict the diffusion coefficients of polymer solutions. On the other hand, the Kirkwood-Riseman theory is more successful because it is based on a more realistic random coil model. Although its application was originally limited to polymer solutions under theta conditions, it has been extended to nontheta conditions (the modified Kirkwood-Riseman equation, see Equation (5-4)). Table 5-1 shows that the predictions of the modified Kirkwood-Riseman theory and the experiment data for PEG in benzene are in good agreement. The difference between the predictions and the data is within 5%.

Table 5-1. Comparison of diffusion coefficients predicted from the modified Kirkwood-Riseman equation with the experimental data for PEG in benzene at 25°C.

	$D_o \times 10^6$ (cm^2/sec)		
M	Kirkwood-Riseman	Experiment (This work)	% difference
440	8.31	8.58	-3.2
960	5.30	5.05	5.0
4250	2.31	2.20	5.0
12600	1.28	1.25	2.4

2. Estimation of k_s

Despite many experimental and theoretical studies, the prediction of k_s still remains a somewhat unsettled problem. Duda et al. [B-51] recently evaluated several existing theories by comparing their predictions with experimental results. They concluded that the Pyun-Fixman theory (versions I and II) was the best theory for predicting k_s at the present time. Still, one should not expect very accurate predictions from this theory. The predictions may differ from the experimental values by as much as 60%, as is the case for the data of Duda et al.

To compensate for the uncertainty of the Pyun-Fixman theory, the parameter λ (see Equation (5-10)) is adjusted to fit the diffusivity data. $\lambda=0.88$ was used to fit the diffusivity data of this work. This compares favorably with $\lambda=0.86$ used by Duda et al. [B-51] to fit the diffusivity data of polystyrene in cyclohexane.

Figure 5-1 is a plot of k_s versus M for PEG in benzene at 25 ^{o}C, predicted by version I of the Pyun-Fixman theory. Note that the application of this theory is originally limited to nonassociating systems. In this work, its application was extended to associating systems by replacing the unimer molecular weight with the apparent molecular weight.

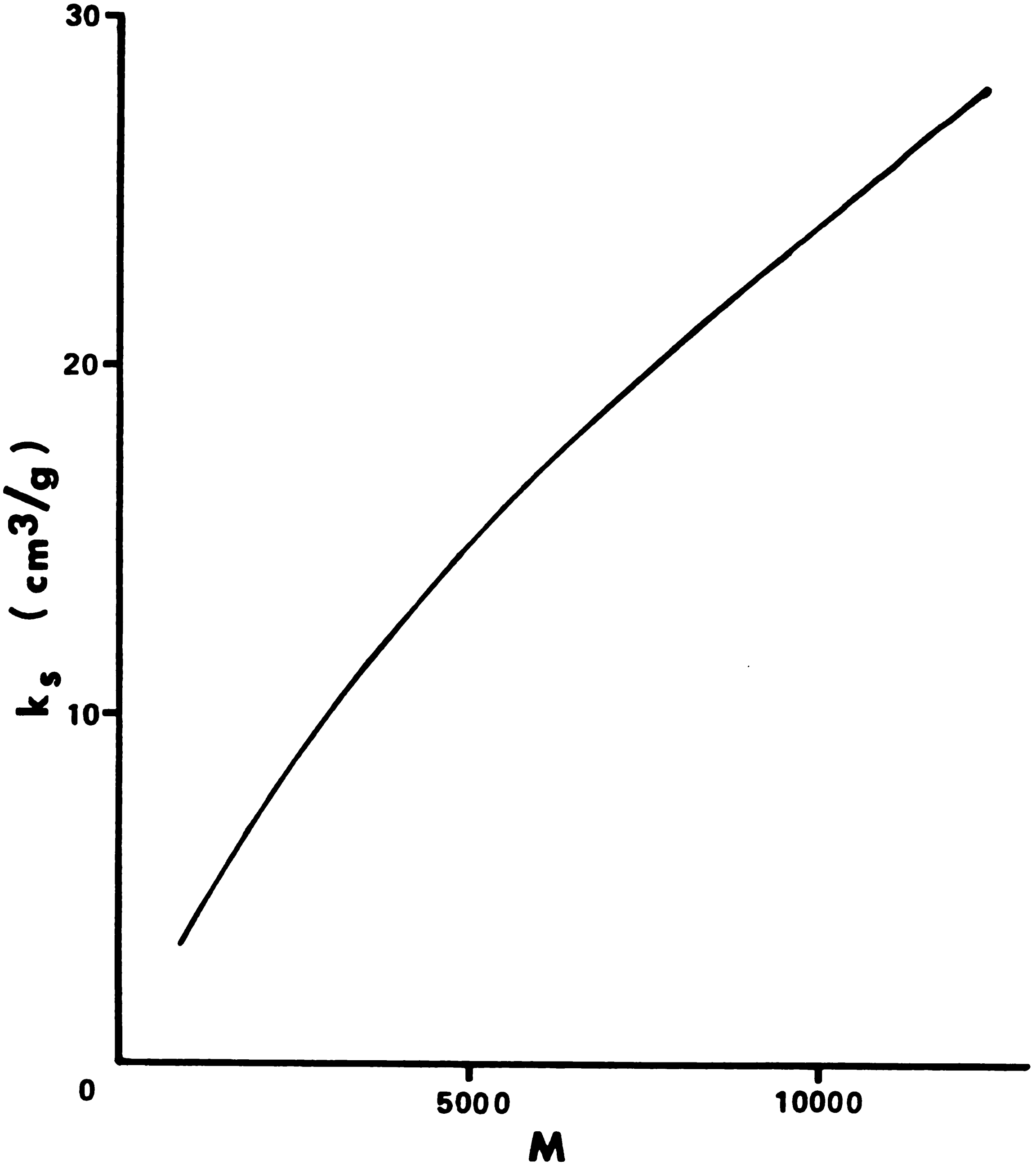


Figure 5-1. k_s versus M for PEG in benzene at 25 °C, predicted by the two-parameter theory (Equation (5-12)).

3. Other Discussions

As shown in Figure 2 (in Part One), the diffusivity data are well described by the association model. The data for the low molecular weight samples (M_1=440, M_1=960) are strongly dependent on concentration due to association. The data for the higher molecular weight samples (M_1=4250, M_1=12600) are less dependent on concentration because the effect of the association term diminishes as molecular weight increases and its effect is also compensated by other terms (A_2 and k_s).

Comparision between predictions from the Pyun-Fixman theory and experimental data was made only for polystyrene in cyclohexane under theta conditions. Thus it is necessary to test this theory and its modified form (the modified Pyun-Fixman theory) more extensively for future work. Accurate knowledge of k_s is vital for predicting diffusion coefficients especially for high molecular weight polymers.

D. Presentation of PTHF Diffusivity Data and Discussions

Diffusivity data for polytetrahydrofuran (PTHF) in five different solvents were measured. They were used to investigate the effects of solvent, molecular weight and temperature on diffusion; to test the Kirkwood-Riseman theory; and to calculate the molecular size of the polymer.

Two sets of PTHF samples were used. The first consisted of three "fresh" PTHF samples purchased recently from Polymer Laboratories, Inc., Massachusetts, and their characteristics are listed in Table 5-2.

Table 5-2. Characteristics of "fresh" PTHF samples.

Molecular weight	Endgroups	Polydispersity
2850	$-CH_3$	< 1.15
30800	$-CH_3$	< 1.10
290000	$-CH_3$	< 1.15

The second set consisted of the "old" PTHF samples used earlier by Lin [B-35]. The adjective "old" was used because these samples were purchased more than three years ago. They were labeled, according to Lin, as PTHF-A1, PTHF-B1 and PTHF-B2, with characteristics listed in Table 5-3. Note that the molecular weights for PTHF-B1 and PTHF-B2 determined by Lin were lower than those by the manufacturer. Lin pointed out that the manufacturer's values were in error because the manufacturer overlooked the fact that these polymers were capable of associating in solution [B-35].

Because Lin did not store the unused portions of these samples (which were later used by this author) under nitrogen nor at very low temperature (as they should be), the characteristics of these polymer samples might have changed over the interim period of time.

Table 5-3. Characteristics of "old" PTHF samples (before degradation). M_M and M_L are respectively the molecular weights determined by the manufacturer and by Lin.

Polymer Code	Endgroups	M_M	M_L
PTHF-A1	$-CH_3$	281,000	----
PTHF-B1	-OH	25,000	7,660
PHTF-B2	-OH	10,200	2,500

Five solvents were used: methylethylketone (MEK), diethylether (DE), n-butanol (BOH), ethylacetate (EA), and bromobenzene (BB). They represent a wide range of solvent power and hydrogen-bonding capability, with characteristics listed in Table 5-4.

Table 5-4. Characteristics of solvents. η_{25} and η_{34} are the viscosities (centipoise) at 25°C and 34°C, respectively. χ is the Flory-Huggin interaction parameter.

Solvent	M.W.	η_{25}	η_{34}	H-Bonding strength	χ
MEK	72	0.40	0.36	Medium	0.40
DE	74	0.23	----	Medium	0.64
BOH	74	2.58	2.05	Strong	1.48
EA	88	0.42	----	Medium	0.38
BB	157	1.06	0.95	Poor	0.61

Diffusion coefficients were measured using the Mach-Zehnder interferometer. A summary of the data is presented in Appendix C. Unless otherwise stated, a polymer solution of 0.30 g/dl was allowed to diffuse into pure solvent at 25°C during each experiment. Thus the average concentration was reported to be 0.15 g/dl. The accuracy of these data was estimated to be within 3%.

1. Effect of solvent

As shown in Appendix C, the diffusion coefficients of PTHF in various solvents decrease in the order DE > MEK > EA > BB > BOH. This trend indicates that polymer molecules diffuse faster in solvents with lower molecular weights (see

Table 5-4). The slow diffusion rate for the polymer molecules in BOH is attributed to the fact that the BOH molecules are capable of associating with each other to form larger clusters.

It is often useful to use the form $D\eta/T$ = f(solute size) as a starting point for correlating diffusivity data. If $D\eta/T$ is plotted against M on a log-log graph, the result can be fitted by a straight line for each solvent, as shown in Figure 5-2. The straight lines are almost parallel with each other, and the quantity $D\eta/T$ decreases in the order MEK > DE > BOH > EA > BB. Note that BOH takes a higher position in the order because the effect of viscosity has been accounted for.

The diffusivity data can also be related by the form $D = G\ M^{-d}$. The estimated values for the parameters G and d are presented in Table 5-5. Recall that the Kirkwood-Riseman theory,

$$(D_o)_\theta = 0.196\ k\ T\ /\ A\ \eta\ M^{0.5} \qquad (5\text{-}19)$$

predicts that the diffusion coefficient should be inversely proportional to the square root of molecular weight. The data in Table 5-5 agree well with this prediction, for the values of d are very close to 0.5.

Figure 5-2. $D\eta/T$ versus M for the "fresh" PTHF samples in various solvents at 25 °C. (▲) MEK; (○) DE; (△) BOH; (●) EA; (▼) BB.

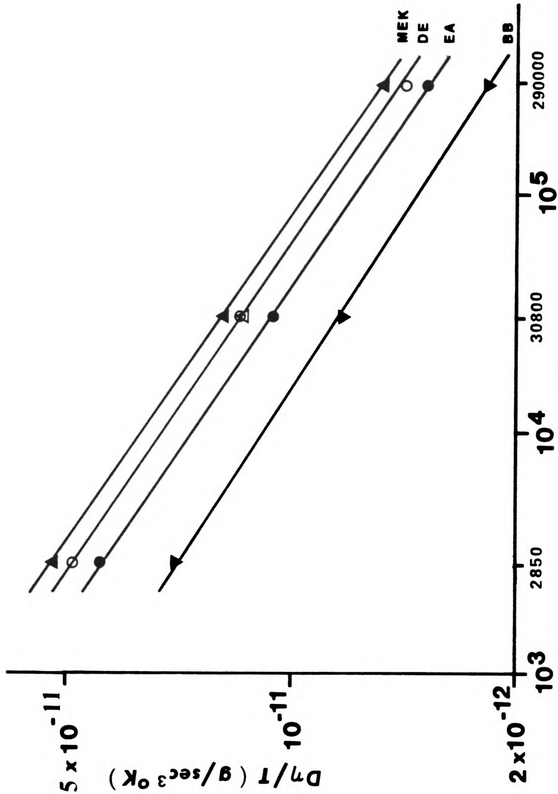

Dη/T (g/sec³ °K)
5 x 10⁻¹¹
10⁻¹¹
2 x 10⁻¹²
10³
2850
10⁴
30800
10⁵
290000
M
MEK
DE
EA
BB

Table 5-5. Parameter estimations for the diffusivity data of "fresh" polymer samples at 25°C using the form $D = G M^{-d}$.

Solvent	$G \times 10^{-4}$	d	Correlation coefficient
MEK	2.134	0.502	-1.00
DE	4.285	0.528	-1.00
EA	1.505	0.503	-1.00
BB	0.296	0.484	-1.00

It is interesting that if $D\eta/T$ is plotted against the solvent molecular weight on a log-log graph, the result fits a straight line for each polymer sample (see Figure 5-3). The slopes of the lines suggest that $D\eta/T$ is inversely proportional to the solvent molecular weight. Wilke and Chang also made the similar correlation for low molecular weight organic liquids and found that $D\eta/T$ was directly proportional to the square root of the solvent molecular weight [B-53]. However, there exists no satisfactory theory for describing the effect of solvent on diffusion in dilute polymer solutions. Further work is needed to determine the correlation between diffusion coefficient and solvent molecular weight.

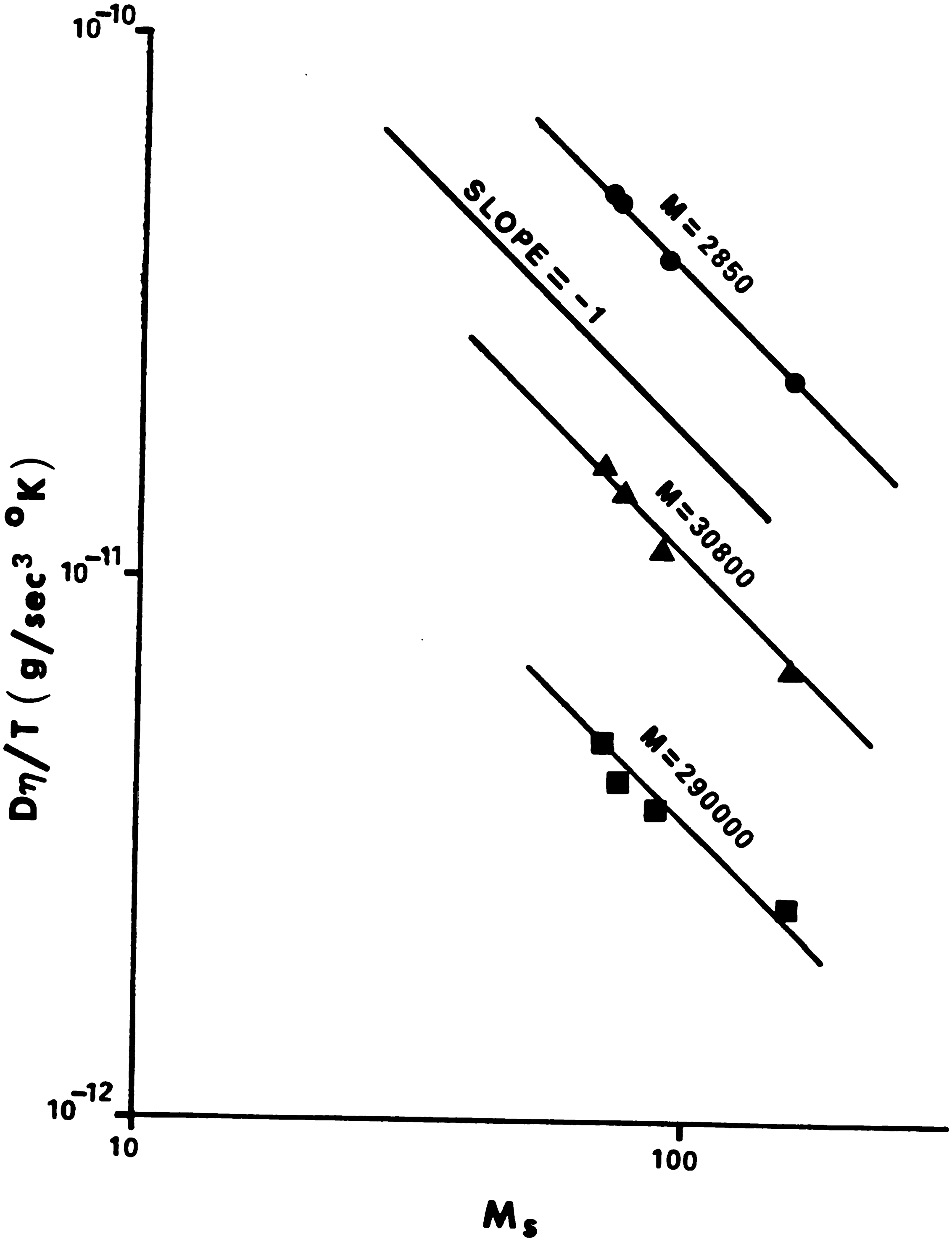


Figure 5-3. $D\eta/T$ versus M_s for the "fresh" PTHF samples at 25 °C. M and M_s are the molecular weights of polymer and solvent, respectivley.

2. Effect of temperature

Figure 5-4 is a plot Dη/T versus M for PTHF in MEK and BB at 25 °C and 34 °C. The variation of temperature appears to have no effect on diffusion for MEK. However its effect is rather significant for BB. Few researches have been conducted for investigating the effect of temperature on diffusion for dilute polymer solutions. Although some researchers suggest that the diffusion coefficient is a peculiar function of the combination of polymer/solvent/temperature, systematic study in this area remains for future work.

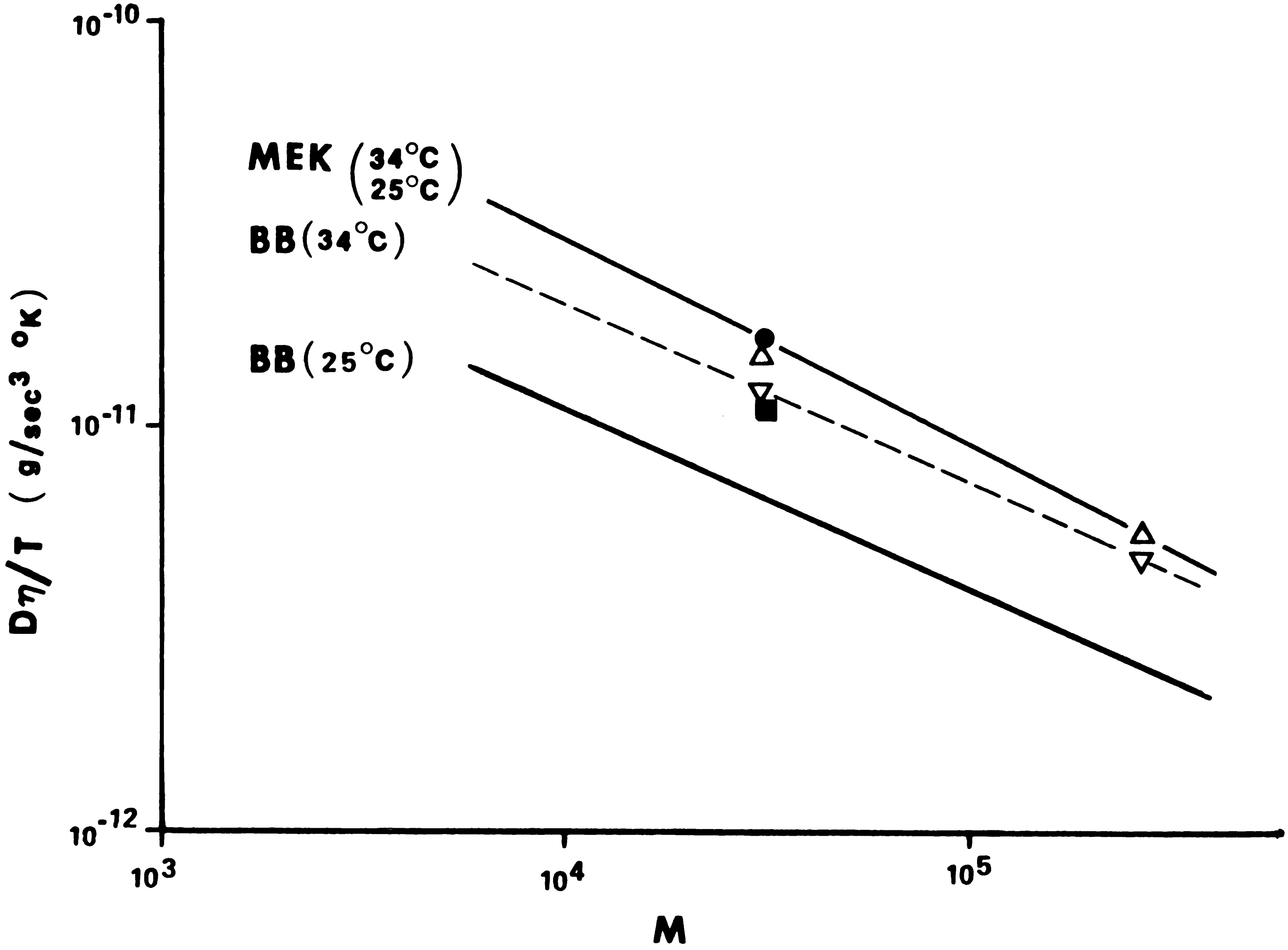
3. Molecular Dimensions

Table 5-6. Estimated values of A (cm) for "fresh" polymer samples.

Solvent	A (25 °C) x 10^9	A (34 °C) x 10^9
MEK	9.6 ± 0.2	9.4 ± 0.1
DE	10.9 ± 0.5	------------
EA	13.1 ± 0.3	------------
BB	21.7 ± 0.5	11.8 ± 0.8

When comparing the equation $D = G\ M^{-d}$ with the Kirkwood-Riseman theory, it can be seen easily that the parameter G is inversely proportional to the parameter A.

Figure 5-4. Comparison of $D\eta/T$ versus M at 25°C and 34°C. △ and ● are data measured by Lin and Yam, respectively, for MEK at 34°C. ▽ and □ are data measured by Lin and Yam, respectively, for BB at 34°C. The solid lines are replotted from Figure 5-2 (at 25°C). The dashed line connects the data of BB at 25°C.


MEK (34°C, 25°C)
BB(34°C)
BB(25°C)
10^{-10}
10^{-11}
10^{-12}
$D\eta/T$ (g/sec^3 °K)
10^3
10^4
10^5
M

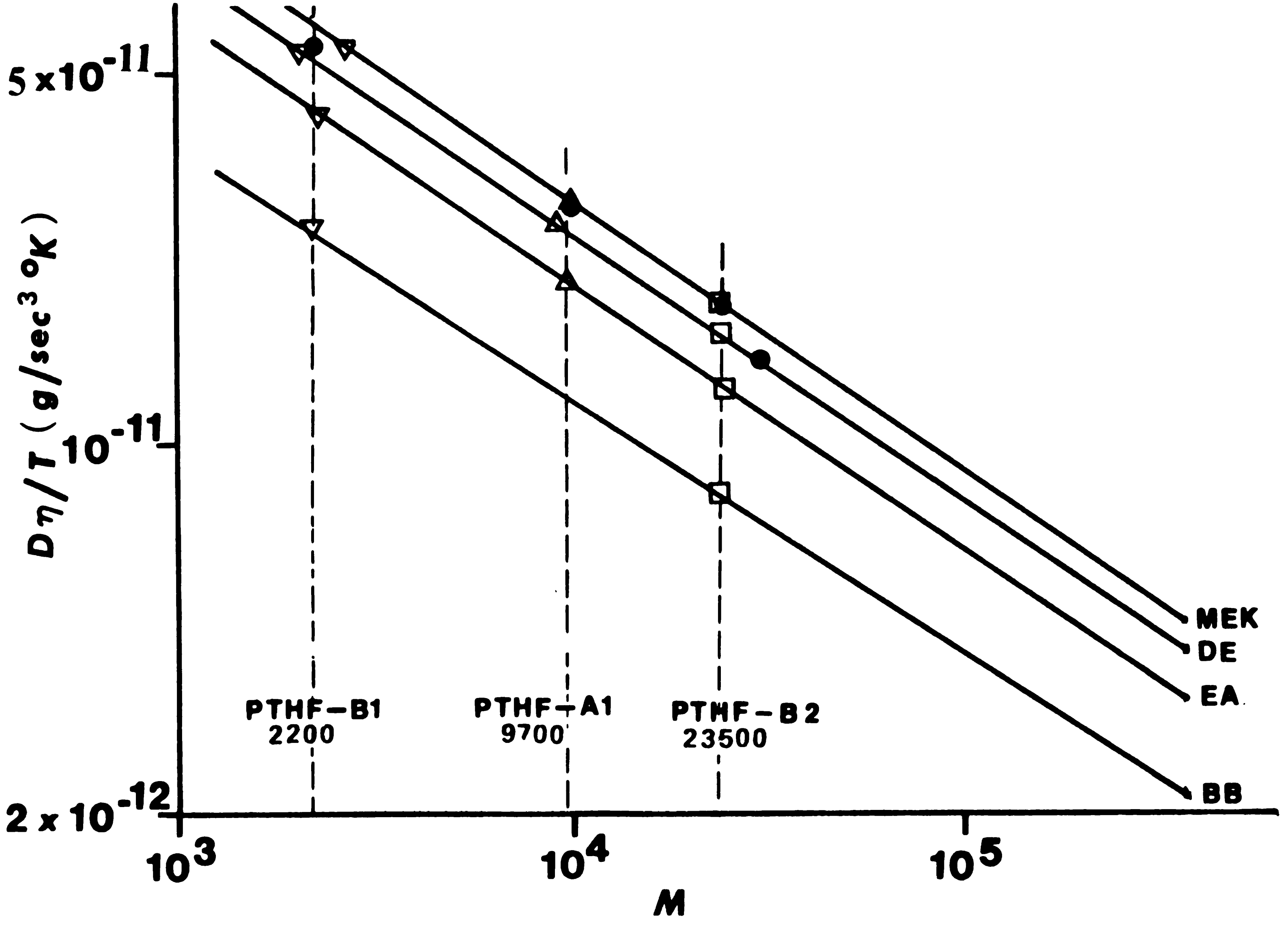
Consequently values for A can be calculated (see Table 5-6). These estimated values are in reasonably good agreement with those reported in the literature [B-9].

4. "Old" Polymer Samples

As mentioned earlier, the "old" polymer samples might have degraded during the time they were not properly stored. The molecular weights for these degraded polymer samples can be estimated using the data from the "fresh" polymer samples. The lines which correlate the diffusivity data (for the "fresh" polymer samples) in Figure 5-2 are redrawn, and the data for the "old" polymer samples are adjusted to fit these lines for each solvent so that they are consistent with the "fresh" polymer data (see Figure 5-5).

Note the that diffusivity data for each polymer falls consistently at a single molecular weight, suggesting that this procedure provides a good measure for the molecular weight of each degraded polymer sample. The molecular weights of PTHF-A1, PTHF-B1 and PTHF-B2 are determined to be 9700, 2200 and 23500, respectively.

Figure 5-5. Estimation of the molecular weights for the "old" polymer samples. △, ▽ and ☐ are the data for PTHF-A1, PTHF-B1 and PTHF-B2, respectively. ● is the data for BOH.


5 x 10^-11
10^-11
2 x 10^-12
Dη/T (g/sec^3 °K)
10^3
10^4
10^5
M
PTHF–B1
2200
PTHF–A1
9700
PTHF–B2
23500
MEK
DE
EA
BB

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The behavior of open associating systems can be described by the measurable quantities: K, ρ, and M_1. The effect of association increases with decreasing molecular weight and is governed by the dimensionless group $P = K\rho/M_1$.

Using the open association model, expressions for osmotic pressure and diffusion coefficient are derived. Predictions from the combination of these expressions and the two-parameter theory are found to compare favorably with the experimental data for PEG in benzene. $(A_2^*)_{obs}$ and $(k_d^*)_{obs}$ differ from their nonassociating counterparts only by K/M_1^2 and K/M_1, respectively. PEG solutions with low polymer molecular weights are affected strongly by association, and their behavior is described by the association model. It is also found that the osmotic pressure is influenced more by association than is the diffusion coefficient.

Although this work deals exclusively with open association, the same procedures for deriving the expressions for osmotic pressure and diffusion coefficient can be used for other types of association.

The following recommendations are proposed for further work:

(1) The application of the association model to diffusion should be tested more extensively. One interesting area arises from some studies which show that the $D(\rho)$ curves display minima, even at dilute concentrations [B-14, B-26, B-35]. This behavior may be explained by the association model. To test this speculation, the concentration dependence of osmotic pressure and diffusion coefficient for these systems should be obtained. The osmotic pressure data are used to match several association models. After a reasonable model is found, an expression for the diffusion coefficient based on this model can be formulated and its predictions tested against the experimental data.

(2) The Pyun-Fixman theory should be tested more extensively. Although some investigators have compared the predictions of this theory with experimental data, their studies are limited to polystyrene under theta conditions. It is desirable to find out how well the modified Pyun-Fixman theory can predict the value for k_s under nontheta conditions. To do this, osmotic pressure and diffusivity data must be obtained for a

dilute polymer solution. For simplicity, it is advisable to start with a nonassociating system. The second virial coefficient A_2 can be obtained from the osmotic pressure data, and the parameter k_d from the diffusivity data. The friction coefficient k_s is calculated using the relation $k_d = 2 A_2 M - k_s - 2 V_{po}$, and the results are compared with the predictions of the modified Pyun-Fixman theory.

NOMENCLATURE

NOMENCLATURE

A	Parameter characterizes the short-range interferences, defined in Equation (4-3)
A_2	Second virial coefficient of a nonassociating polymer solution, defined in Equation (13)
A_{21}	Second virial coefficient of the unimer
$A_{2,n}$	Second virial coefficient of a monodisperse polymer with molecular weight equal to the number average molecular weight of a multimer mixture
A_2^*	Second virial coefficient of an associating polymer polymer solution, defined in Equation (4-16)
$(A_2^*)_{obs}$	Observed second virial coefficient defined in Equation (16)
A_{ij}	Interaction between a pair of polymer molecules i and j at infinite dilution, defined in Equation (14)
B	Parameter characterizes the long-range interferences
B_i	i-mer
BB	Bromobenzene
BOH	n-butanol
C_1	Molar concentration of unimer
C_i	Molar concentration of i-mer
C_p	Molar concentration of polymer solute
D	Diffusion coefficient of a nonassociating polymer polymer solution

D_o	Diffusion coefficient at infinite dilution
$(D_o)_\theta$	Diffusion coefficient at infinite dilution under theta conditions
D^*	Diffusion coefficient of an associating polymer polymer solution
DE	Diethyl ether
EA	Ethyl acetate
f	Friction coefficient defined in Equation (5-7)
ΔG_m	Change in free energy of mixing
J	Total number of fringes
K	Association equilibrium constant
K'	Constant defined in Equation (6-4)
K_v	Parameter in Equation (27)
k	Boltzmann's constant
k_d	Concentration dependence of diffusion coefficient defined in Equation (5-2)
k_d^*	Concentration dependence of diffusion coefficient for an associating polymer solution
$(k_d^*)_{obs}$	Observed k_d^* (see Equation (25))
k_s	Coefficient defined in Equation (20)
M	Molecular weight for monodisperse polymer
M_1	Molecular weight of unimer
M_a	Apparent polymer molecular weight
M_n	Number average molecular weight
M_s	Molecular weight of solvent
M_w	Weight average molecular weight
MEK	Methyl ethyl ketone
m	Ratio of molar volumes of polymer to solvent

N_a	Avogadro's number
n	Number of moles
P	Dimensionless polymer concentration for an associating polymer solution, defined in Equation (9)
PEG	Polyethylene glycol
PTHF	Polytetrahydrofuran
R	Gas constant
$\langle R^2\rangle_o$	Unperturbed mean-square end-to-end distance
$\langle S^2\rangle_o$	Unperturbed mean-square radius of gyration
T	Absolute temperature
u	Excluded volume per sphere
V_p	Partial specific volume of polymer
V_{po}	Partial specific volume of polymer at infinite dilution defined in Equation (19)
w_i	Weight fraction of polymer i
z	Excluded volume parameter (see Equation (4-7)
$\bar{z}$	Parameter related to z, defined in Equation (4-26)

Greek symbols

α	Exponent in Equation (4-13)
α_s	Expansion coefficient defined in Equation (4-4)
β	Exponent in Equation (4-8)
γ	Exponent in Equation (29)
δ	Solubility parameter
ζ	Dimensionless group defined in Equation (2-7)

η	Viscosity of solvent
$[\eta]$	Intrinsic viscosity
λ	Ratio of $D_{o,exptl}$ to $D_{o,theory}$
μ_s	Chemical potential of solvent in solution
μ_s^o	Chemical potential of pure solvent
ξ	Dimensionless group defined in Equation (8)
π	Osmotic pressure for a nonassociating polymer solution
π^*	Osmotic pressure for an associating polymer solution
Π	Dimensionless osmotic pressure defined in Equation (15)
ρ	Polymer mass concentration
ρ_s	Solvent mass concentration
ϕ	Volume fraction
χ	Flory-Huggins interaction parameter
Ψ_1	Dimensionless group defined in Equation (4)
Ψ_2	Dimensionless group defined in Equation (24)

Subscripts

p	Polymer
s	Solvent
θ	Under theta conditions
o	At infinite dilution

Superscript

*	Relating to open association

APPENDICES

APPENDIX A

SAMPLE CALCULATION

APPENDIX A

SAMPLE CALCULATION

Polymer: PEG (M=960)

Solvent: benzene

Temperature: 25 °C

Solution A (for the upper level)
Pure benzene

Solution B (for the lower level
Concentration = 0.400 g/dl

Below is the calculation for determining the diffusion coefficient for the above system. The distances on the photographic plate were measured using an optical comparator made from a microscope fitted with a travelling eyepiece. The nomenclature used by Bidlack [B-5] is followed here.

Exposure number	Time, minutes
1	0
2	5
3	10
4	15
5	20
6	25

$J = 4.6$

Exposure	j	$(x_o' - x_j)$, cm	k	$(x_o' + x_k)$, cm
1	1	0.0937	3	0.2220
2	1	0.1069	3	0.2817
3	1	0.1220	3	0.3383
4	1	0.1664	3	0.4170
5	1	0.1532	3	0.4280
6	1	0.1290	3	0.4295

The measurements were fed into a computer program for calculating the diffusion coefficient. A plot showing the goodness of the data is shown in Figure A-1. All the data points lie on a straight line. The diffusion coefficient for this run was calculated to be 4.84×10^6 cm^2/sec.

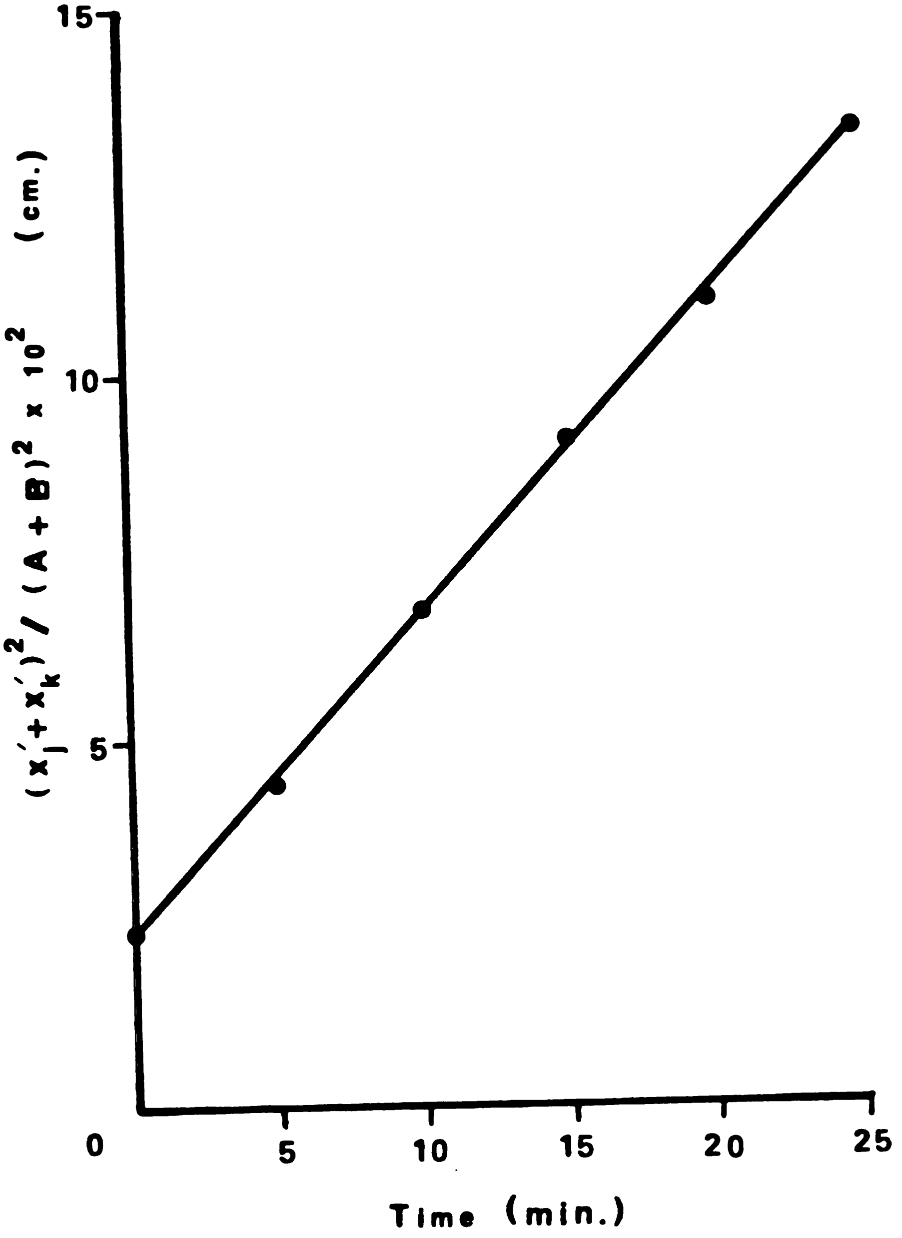


Figure A-1. Sample calculation for the diffusion coefficient of PEG in benzene. The symbols are those used by Bidlack [B-5].

APPENDIX B

DIFFUSIVITY DATA OF PEG

APPENDIX B

DIFFUSIVITY DATA FOR PEG IN BENZENE

Polymer: Polyethylene glycol (PEG)

Solvent: Benzene

Temperature: 25 °C

M1=440

$\rho \times 10^2$ (g/ml)	$D \times 10^6$ (cm^2/s)
0.20	7.94
0.20	8.39
0.60	7.68
0.60	7.45
1.00	6.96
1.00	6.72
1.45	6.51
1.80	6.15
2.00	5.75

M1=960

$\rho \times 10^2$ (g/ml)	$D \times 10^6$ (cm^2/s)
0.20	4.84
0.20	5.10
0.20	4.79
0.60	4.62
1.00	4.37
1.40	4.26
1.40	4.10
1.85	3.99
2.00	3.97
2.00	3.73

M1=4250

$\rho \times 10^2$ (g/ml)	$D \times 10^6$ (cm^2/s)
0.20	2.20
0.20	2.09
0.60	2.09
0.60	2.01
1.00	1.99
1.00	1.94
1.40	2.01
1.80	1.90
2.00	1.82
2.00	1.88

M1=12600

$\rho \times 10^2$ (g/ml)	$D \times 10^6$ (cm^2/s)
0.20	1.22
0.20	1.14
0.60	1.07
0.60	1.15
1.00	1.08
1.00	1.02
1.40	1.09
1.80	1.02
2.00	0.99

APPENDIX C

DIFFUSIVITY DATA OF PTHF

APPENDIX C

DIFFUSIVITY DATA FOR PTHF IN VARIOUS SOLVENTS

Tables C-1. Diffusivity data (cm^2/sec) of "fresh" PTHF samples measured using the Mach-Zehnder interferometer in various solvents. Unless otherwise stated, 0.3 g/dl of solutioon was allowed to diffuse into pure solvent at 25 ^oC, and the concentration for the diffusion measurements was reported to be 0.15 g/dl.

M	Solvent	$D \times 10^7$	$D/T \times 10^{11}$
2850	DE	63.1	4.87
	MEK	38.7	5.20
	EA	27.8	3.92
	BB	6.47	2.30
30800	DE	19.0	1.47
	MEK	12.2	1.64
(T = 34 ^oC)		13.9	1.63
	EA	8.19	1.15
	BB	1.92	0.687
(T = 34 ^oC)	BB	3.51	1.09
	BOH	1.65	1.43
290000	DE	5.52	0.426
	MEK	3.80	0.510
	EA	2.72	0.383
	BB	0.688	0.245

Tables C-2. Diffusivity data (cm^2/sec) of "old" PTHF samples measured using the Mach-Zehnder interferometer in various solvents. Unless otherwise stated, 0.3 g/dl of solutioon was allowed to diffuse into pure solvent at 25 °C, and the concentration for the diffusion measurements was reported to be 0.15 g/dl.

M	Solvent	D x 10^7	D /T x 10^{11}
PTHF-A1	DE	35.1	2.71
		3.37	2.60
	MEK	21.6	2.90
		23.7	3.19
(T = 34 °C)		4.31	5.05
	EA	14.3	2.02
	BOH	34.3	2.97
PTHF-B1	DE	72.6	5.60
	MEK	43.5	5.84
	EA	29.4	4.15
	BB	7.17	2.55
	BOH	6.90	5.97
PTHF-B2	DE	21.2	1.64
	MEK	13.8	1.85
	EA	9.22	1.30
	BB	2.27	0.807
	BOH	2.13	1.85
(C = 0.2 g/dl)		3.17	2.74

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