THERMODYNAMICS AND DIFFUSION IN POLYMER SOLUTIONS CONTAINING ASSOCIATING SPECIES

By

Joe Su-Shien Lin

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1980

ABSTRACT

THERMODYNAMICS AND DIFFUSION IN POLYMER SOLUTIONS CONTAINING ASSOCIATING SPECIES

By

Joe Su-Shien Lin

Thermodynamic and diffusion data of polymer-solvent systems in the literature indicate that agreement between theory and experiment is far from satisfactory. One type of polymer solution which offers interesting insights and for which little has been published is the associating polymer solute in dilute solution. Although association and/or strong intermolecular interactions have been cited by a few researchers as the cause of otherwise unexplainable experimental results, little effort has been made to study the effects of association of polymer molecules on solution properties. As a result, there exists at present no satisfactory theory which describes accurately the thermodynamic and diffusion properties of polymer solutions containing associating species.

An association theory is proposed in this work to describe the thermodynamic and diffusion properties of dilute solutions of an associating polymer solute in an inert solvent. Application of the association theory leads to the prediction that the osmotic pressure of a dilute solution containing associating polymer solute can be expressed as:

$$\frac{\Pi}{RT} = \frac{1}{\underline{V} - B} - \frac{K/\alpha}{\underline{V}^2}$$

which is similar to the van der Waals equation not only in form but also in the physical significance of the corresponding parameters. The term $(K/\alpha)/\underline{V}^2$ accounts for effects of intermolecular attraction between polymer molecules and the parameter B represents molar excluded-volume of polymer molecules in solution. The theory also suggests that the experimentally observed osmotic second virial coefficient can be split into two parts: (1) The "true" second virial coefficient which is directly related to the excluded-volume of polymer molecules and (2) An association term which accounts for the effects of association.

Based on the same theory, the concentration dependence of the diffusion coefficient of such a solution can be described by the equation:

$$D = D^\circ \chi_{asso}(1 + k_d^m \rho_p + \ldots)$$

where χ_{asso} is a complex function of polymer concentration that reflects the variation of the average size of diffusing species due to intermolecular association. The equation correctly predicts that the diffusion rate first decreases sharply with concentration and then attains an almost constant value or passes through a shallow minimum depending on the magnitudes of the thermodynamic and hydrodynamic interactions between solution components.

Joe Su-Shien Lin

A Mach-Zehnder diffusiometer was used to measure the diffusion coefficients of eight polymer-solvent mixtures at 34.0°C. Osmotic pressures and osmotic second virial coefficients at 34.0°C were determined with a Hallikainen automatic membrane osmometer. Monodisperse ($M_W/M_N < 1.05$) polytetrahydrofurane (PTHF) with and without OH end-groups were chosen for this work. Two solvents (bromobenzene and methyl-ethyl-ketone) having different capability for blocking the formation of hydrogen bonds were employed to study the solvent influence upon association behavior.

The experimental results indicate that the OH end-groups indeed affect thermodynamic and diffusion properties of dilute polymer solutions significantly. Data from this work as well as from the literature are used to test the validity of the association model with good results.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Donald K. Anderson for his guidance and continued support during the course of this work.

Grateful thanks are extended to Dr. Robert F. Blanks for suggesting this problem and for his continuing encouragement.

The author is indebted to the Division of Engineering Research of the College of Engineering at Michigan State University and to the Amoco Foundation for providing financial support.

Special thanks are due to Dr. Hans G. Elias and Dr. Karl Sǒlc of Michigan Molecular Institute whose useful discussions and generous assistance are invaluable to the completion of this work.

The understanding, support and encouragement of the author's family, especially his mother, is gratefully appreciated.

TABLE OF CONTENTS

LIST OF TABLES v

LIST OF FIGURES vi

I. INTRODUCTION 1

II. THEORETICAL BACKGROUND 5

A. Thermodynamics of Polymer Solutions 5

1. Flory-Huggins Theory 7
2. Corresponding States Theory 13
3. Solubility Parameter Theory 20
4. Excluded Volume Theory 23

B. Diffusion in Polymer Solutions 27

1. Diffusion in Infinitely Dilute Polymer Solutions 29

a. The Kirkwood-Riseman Theory 29
b. Flory's Theory 31
c. Johnston's Theory 35
d. Fedors' Empirical Relation 37

2. Diffusion in Dilute Polymer Solutions 39

III. EXPERIMENTAL METHOD FOR MEASURING OSMOTIC PRESSURES OF DILUTE POLYMER SOLUTIONS 41

A. Experimental Aparatus and Principle of Operation 41
B. Membrane Conditioning 44
C. Experimental Procedure 46
D. Error Analysis 49

IV. EXPERIMENTAL METHOD FOR MEASURING DIFFUSION COEFFICIENTS OF DILUTE POLYMER SOLUTIONS 50

A. Experimental Apparatus 50
B. Experimental Procedure 58
C. Theory and Calculations 62
D. Calibration 67
E. Error Analysis 69

V. THERMODYNAMICS OF ASSOCIATING POLYMER SOLUTIONS .. 70

A. Methods for Detecting Association of Polymer Molecules in Dilute Solutions 70
B. Types of Association in Polymer Solutions 73
C. Thermodynamics of Solutions Containing Association Polymer Species 76
D. Presentation of Osmometry Data and Discussions 87

VI. DIFFUSION IN ASSOCIATING POLYMER SOLUTIONS 101

A. Thermodynamic Basis of Diffusion in Solutions 101
B. Theory of Diffusion in Solutions Containing Associating Polymer Solutes 107
C. Presentation of Interferometry Diffusion Data and Discussions 118

VII. CONCLUSIONS AND RECOMMENDATIONS 132

NOMENCLATURE 135

APPENDICES 142

BIBLIOGRAPHY 150

LIST OF TABLES

I. Results of the Calibration Runs on the Interferometer.................................. 68

II. Characteristics of PTHF Samples 87

III. Concentration Dependence of Reciprocal Apparent Number Average Molecular Weights of PTHF-A2-MEK Solutions at 34.0°C 88

IV. Concentration Dependence of Reciprocal Apparent Number Average Molecular Weights of PTHF-B1-MEK Solutions at 34.0°C 89

V. Summary of Diffusion Coefficient Data for PTHF-Solvent Systems at 34.0°C 125

LIST OF FIGURES

Figure

1A A Free-Draining Molecule During Translation Through Solvent 33

1B Translation of a Chain Molecule with Perturbation of Solvent Flow Relative to the Molecule 33

2 Schematic Flow Diagram of Hallikainen Automatic Membrane Osmometer 43

3 Schematic Diagram of Interferometer Showing Position of Mirrors 51

4 Photograph of Mach-Zehnder Interferometer Showing Components 52

5 Photograph of Diffusion Cell for Measurement of Diffusion Coefficients 55

6 Diagram of Diffusion Cell 56

7 Typical Set of Photographs Taken During Diffusion Run 61

8 Diffusion Cell Coordinates 62

9 Fringe Pattern 63

10 Concentration Dependence of Reciprocal Apparent Number Average Molecular Weights of PTHF-MEK Solutions at 34.0°C 90

11 Molecular Weight Dependence of Observed Osmotic Second Virial Coefficients of PEG Solutions 95

12 Comparison of Osmotic Pressure Data Fittings Based on Various Solution Theories for PTHF-B1-MEK Solution at 34.0°C 98

Figure

13 Concentration Dependence of D/D^0, χ_{asso} and $(1+k_d^m\rho_p+ \ldots)$. $D=D^0\ \chi_{asso}(1+k_d^m\rho_p+..)$ 115

14 Concentration Dependence of Diffusion Coefficients of Non-Associating PTHF Solutions at 34.0°C 119

15 Concentration Dependence of Diffusion Coefficients of Associating PTHF-MEK Solutions at 34.0°C 121

16 Concentration Dependence of Diffusion Coefficients of Associating PTHF-BB Solutions at 34.0°C 123

17 Correlations Between Experimental D^0 Values of PTHF-Solvent Systems and Fedors' Empirical Relation 129

I. INTRODUCTION

The dependence of the rate of diffusion of polymer molecules on concentration has long been of considerable empirical and theoretical interest. However, present understanding of the diffusion process in polymer-solvent systems is far from satisfactory, and estimates of diffusion coefficients are often unreliable except in some limiting cases such as in infinitely dilute solutions of nonassociating solutes. Although methods are available for predicting the concentration dependence of diffusion coefficients in dilute polymer solutions, they are for the most part valid only for non-electrolyte, non-polar polymer solutions. This situation results in large part from the lack of a usable kinetic theory of polymer solutions and from the lack of reliable experimental data. Difficulties in understanding polymer solution behavior arise from the complex nature of polymer molecules (e.g., the enormous size and very large number of internal degrees of freedom of polymer chains, the polydispersity of polymer samples, etc.).

Using irreversible thermodynamics as a theoretical basis for description, two factors contribute to the rate of diffusion of polymer molecules in solution: (1) A thermodynamic factor which is related to the driving force of the diffusion process, and (2) A hydrodynamic factor which describes the resistance to movement of diffusing components through the surrounding medium. The concentration dependence of diffusion rate is, therefore, determined by the concentration dependence of these two factors. Although methods for predicting the concentration dependence of diffusion coefficients in polymer solutions from thermodynamic and hydrodynamic properties have been available for some time, a recent and probably the most rigorous method was proposed by Vrentas and Duda [1A-1]. Their result suggests that the diffusion coefficient is a linear function of concentration in the dilute concentration region and that the concentration dependence of diffusion coefficient is determined not only by thermodynamic and hydrodynamic factors, but also by volumetric effects due to the mixing process. The predicted concentration dependence of the diffusion coefficient according to the method proposed by Vrentas and Duda is generally in good agreement with experimental data. Diffusion data in the literature indicate that the only exceptions are those polymer-solvent mixtures in which association or strong intermolecular interaction occurs [1A-2, 3, 4].

Disagreement between theory and experiment can be found not only in diffusional properties, but also in the thermodynamics of dilute polymer solutions. For example, the well-known excluded volume theory of dilute polymer solution predicts that the osmotic second virial coefficient should decrease slowly with increasing polymer molecular weight. This prediction is generally obeyed by a great number of polymer-solvent systems. However, in some cases the observed osmotic second virial coefficients are found to decrease or even change sign with decreasing molecular weight. It has been suggested [1A-5, 6] that this inconsistency, like those observed for the transport properties of dilute polymer solutions, is caused by intermolecular association between polymer molecules in solution.

Historically, the concept of associating organic compounds has been largely ignored throughout the development of polymer physics. The reasons for that can be traced back to the very beginning of the discovery of macromolecules. The idea that macromolecules themselves are associates of smaller organic colloids was dismissed so thoroughly about fifty years ago [1A-7], that very few investigators have reconsidered association as an important phenomena in polymer solutions. Furthermore, the theories of polymer solutions as developed by Flory and Huggins [1A-8] appeared to explain solution properties very well without the assumption of association. As a result, the idea of intermolecular association in polymer solution became unattractive and not very useful to polymer researchers. Nevertheless, as macromolecular solutions have been studied more extensively in the past decade, much evidence indicates that there are many polymers which associate with themselves in solution and existing theories which do not take the effects of this association into account are often inadequate to describe solution properties.

This work is aimed at studying the effects of intermolecular association on the concentration dependence of thermodynamic and diffusion properties in polymer solutions. An association model, which takes into consideration intermolecular association, is proposed by the author and the advantages of this theory over non-association theories are discussed. Data for osmotic pressures and diffusion behaviors from this work as well as from the literature are used to test the validity of the association model with good results.

II. THEORETICAL BACKGROUND

A. Thermodynamics of Polymer Solutions

Raoult's law is often used as a convenient reference state to which the thermodynamic properties of solutions can be compared. Ideal solution behavior requires that the following two conditions be fulfilled:

The entropy of mixing is given by

$$\Delta S_m^I = - R \ (n_1 \ln X_1 + n_2 \ln X_2) \qquad \text{(II-1)}$$

where n_i and X_i are the number of moles and mole fraction of component i, respectively, and the superscript I indicates the solution is ideal; and,

The heat of mixing is zero.

$$\Delta H_m^I = 0 \qquad \text{(II-2)}$$

Deviations from ideality may arise from failure of either of these conditions. Traditional ideas about non-ideality of solution properties concentrated on the dissimilarity of interaction energies between solute and solvent molecules of "different chemical nature." This eventually led to the concept of the "regular solution" which in turn serves as a starting point for the investigation of polymer solution properties.

The "regular" solution was first introduced by Hildebrand [2A-1] to characterize solutions which possess the entropy of mixing of an ideal solution. By inspecting experimental data of several mixtures, Hildebrand [2A-2] concluded that for most mixtures, except those in the neighborhood of the critical point, thermal agitation causes practically random mixing and thus the primary requirement for the formation of regular solutions is fulfilled. In solutions with non-vanishing heats of mixing, Hildebrand argued, the excess entropy of mixing at constant pressure (due to volume expansion) is balanced by the corresponding enthalpy of mixing and consequently, both corrections can be neglected in calculating isothermal excess free energy. In seeking an explanation for the departure of actual solutions from regular behavior, it is therefore of importance to study the influence of deviations from "random distribution" on the thermodynamic functions of the system. (By random distribution we mean that the local composition is identical with the bulk composition of the solution.)

It has been well known that polymer solutions show extremely large deviations from ideal solution behavior. Excess thermodynamic properties remain large even if the heat of mixing of the solution is negligible. This observation led to the conclusion that polymer solutions are characterized by large excess entropies of dilution, mainly due to the great difference in size between polymer and solvent molecules.

Polymer solutions differ from mixtures of spherical solute and solvent particles by the linking of the solute particles into polymer chains. The number of ways of arranging segments of polymer chains in solution is, of course, different from that of arranging spherical solute molecules, and hence no longer gives the ideal entropy of mixing. Polymer solution thermodynamics usually deals with the effect of chain connectivity on the thermodynamic properties of solutions. In fact, a large part of the development of polymer solution thermodynamics has been centered on the effects of the difference in size between polymer and solvent molecules.

1. Flory-Huggins Theory

The Flory-Huggins Theory [2A-3] of polymer solutions originates with and conserves important features of the theory of regular solutions for mixtures of spherical molecules of equal size. According to classical thermodynamics of solutions, the free energy of mixing is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad \text{(II-3)}$$

Thus, one approach to understanding the thermodynamics of polymer solutions is to consider methods of calculating ΔH_m, the heat of mixing, and ΔS_m, the entropy of mixing.

The heat of mixing is related to the formation in the mixture of contacts of a new type, (A-B), which replace some of the (A-A) and (B-B) contacts of the pure components according to the quasi-chemical process:

$$\tfrac{1}{2}(A\text{-}A) + \tfrac{1}{2}(B\text{-}B) \rightarrow (A\text{-}B) \qquad \text{(II-4)}$$

ΔH_m is thus proportional to an interchange energy (Δw), which is in turn related to the energy ε_{ij} required to break and form the contacts in equation (II-4):

$$\Delta H_m \propto \Delta w = \tfrac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB} \qquad \text{(II-5)}$$

By assuming a lattice model,* Flory was able to derive the following equation for the entropy of athermal mixing:

$$\Delta S_m = -k\,(n_1 \ln\phi_1 + n_2 \ln\phi_2) \qquad \text{(II-6)}$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer solute, respectively, and are defined by equations (II-7):

$$\phi_1 = n_1/(n_1 + r\,n_2) \qquad \text{(II-7a)}$$

$$\phi_2 = r\,n_2/(n_1 + r\,n_2) \qquad \text{(II-7b)}$$

Here r is the ratio of partial molar volume of polymer

---

* Huggins [2A-4] reached the same conclusion as the result of Flory's without the assumption of fluid lattice.

solute to that of solvent and n_1 and n_2 are the number of molecules of solvent and solute, respectively. The entropy of mixing expressed by equation (II-6) is just the configurational or combinatorial entropy associated with the large number of ways of arranging the segments of polymer chain molecules and solvent molecules. It depends only on the concentration of the mixture and does not take into account that effects caused by the difference in structural and chemical nature between polymer and solvent molecules.

In ΔG_m it is only ΔH_m which depends on the nature of the molecules (according to the original Flory-Huggins Theory), which is characterized by the dimensionless parameter:

$$\chi_1 = Z\,\Delta w/k\ T \qquad \text{(II-8)}$$

Here Z is the lattice coordination number. According to Flory, ΔH_m can be expressed by:

$$\Delta H_m = k\ T\ \chi_1\ n_1\ \phi_2 \qquad \text{(II-9)}$$

Substituting equation (II-6) and (II-9) into equation (II-3), one gets:

$$\Delta G_m = k\ T(n_1\ \ln\phi_1 + n_2\ \ln\phi_2 + \chi_1\ n_1\ \phi_2) \qquad \text{(II-10)}$$

It was soon found experimentally that χ_1, as determined from vapor pressure measurements of ΔG_m, was not the same as found from ΔH_m. To account for this, Δw was interpreted [2A-5] to be an interchange free energy with enthalpic and entropic contributions, i.e.,

$$\Delta w \rightarrow \Delta w_G = \Delta w_H - T\Delta w_S$$

and $$\chi_1 = \chi_H + \chi_S = z\Delta w_H/k\ T - z\Delta w_S/k \qquad \text{(II-11)}$$

Equation (II-11) suggests that χ_1 varies inversely with temperature if both Δw_H and Δw_S are independent of temperature. An important assumption of the theory is that volume changes taking place during mixing, ΔV_m, are neglected. Thus, not only is the total ΔV_m zero, but so are any volume effects on the heat and entropy of mixing. Experimental results [2A-6] also showed that the entropic contribution, χ_S, is dominant compared to the enthalpic contribution χ_H. It becomes clear that the noncombinatorial entropy of mixing, which may be caused by the different chemical nature and/or difference of size between polymer and solvent molecules, is extremely significant to polymer mixtures and can be considered as a characteristic property of polymer solutions.

It is convenient to study thermodynamics of polymer-solvent systems by measuring the change of chemical potential of the solvent in solution due to the addition of an infinitesimal amount of polymer solute. Differentiation of equation (II-10) for ΔG_m with respect to n_1 and multiplication of the result by Avagadro's number N_A gives:

$$\mu_1 - \mu_1^0 = R\ T(\ln(1 - \phi_2) + (1 - r^{-1})\ \phi_2 + \chi_1\phi_2^2) \qquad \text{(II-12)}$$

where μ_1 is the chemical potential of the solvent in the solution and μ_1^0 the chemical potential of the pure solvent. By using a series expansion of $\ln(1 - \phi_2)$, equation (II-12) can be rewritten:

$$\mu_1 - \mu_1^0 = -\ R\ T(\phi_2/r + (\tfrac{1}{2} - \chi_1)\ \phi_2^2 + \phi_2^3/3 + ---) \qquad \text{(II-13)}$$

The sum of the second and higher order terms of ϕ_2 in equation (II-13) is defined by Flory as the "excess relative chemical potential" of the solvent:

$$(\mu_1 - \mu_1^0)_E = -\ R\ T((\tfrac{1}{2} - \chi_1)\ \phi_2^2 + \phi_2^3/3 + ---) \qquad \text{(II-14)}$$

In general, the excess function $(\mu_1 - \mu_1^0)_E$ has two contributions, namely enthalpic and entropic contributions. Therefore equation (II-14) can be generalized (with neglect of ϕ_2^3 and higher order terms) as:

$$(\mu_1 - \mu_1^0)_E = R\ T(k_1 - \Psi_1)\ \phi_2^2 \qquad \text{(II-15)}$$

Here k_1 and Ψ_1 are introduced as energy and entropy parameters such that:

$$\overline{\Delta H_1} = R\ T\ k_1\ \phi_2^2 \quad ; \quad \overline{\Delta S_1} = R\ \Psi_1\ \phi_2^2 \qquad \text{(II-16)}$$

The interaction parameter of the preceding treatment χ_1 may then be related to these parameters by comparing equations

(II-14) and (II-15), i.e.,

$$k_1 - \Psi_1 = \chi_1 - \tfrac{1}{2} = \chi_H - (\tfrac{1}{2} - \chi_S) \qquad \text{(II-17)}$$

A characteristic parameter of polymer solution can then be defined as:

$$\theta = k_1 \, T/\Psi_1 \qquad \text{(II-18)}$$

Hence the excess chemical potential may be rewritten as:

$$(\mu_1 - \mu_1^0)_E = - R\,T(1 - \theta/T)\,\phi_2^2 \qquad \text{(II-19)}$$

Equation (II-19) predicts that the excess chemical potential of the solvent vanishes when the solution is at "theta" condition, i.e., $T = \theta$. Under this special condition, the enthalpic and entropic effects compensate each other, and the interaction parameter χ_1 has a value of 0.5.

Despite the fact that the Flory-Huggins Theory fails to explain many important features of polymer solution thermodynamics [2A-6], the theory has been applied very extensively because of its simplicity. The Flory-Huggins Theory serves as an excellent reference state for polymer solutions just as ideal solution theory is used as a reference state for small molecule solutions.

2. Corresponding States Theory

The principle of corresponding states of pure liquids rests on the assumption that the potential energy of attraction of a pair of molecules, ε, can be expressed by some universal function ψ (possibly the often used 6-12 potential function) together with two characteristic factors d^*, ε^* of the molecular species.

$$\varepsilon(d) = \varepsilon^* \psi(d/d^*) \qquad \text{(II-20)}$$

Here d is the distance between two interacting molecules and the scale factors ε^*, d^* represent the coordinates of the minimum of $\varepsilon(d)$. Thus, the properties of a given liquid can in principle be determined (if the universal function is known) by these two parameters. The parameters are conveniently embodied in a characteristic temperature T^* and a characteristic pressure P^*. For monomeric liquids, they are commonly expressed as:

$$\begin{aligned} T^* &= \varepsilon^*/k \\ P^* &= \varepsilon^*/d^{*3} \end{aligned} \qquad \text{(II-21)}$$

where k is the Boltzmann constant. Prigogine and collaborators [2A-7] assumed that the principle of corresponding states was also obeyed by polymeric liquids with a polymer molecule considered as a succession of quasi-spherical segments. For polymeric liquids, it is predicted that the contact between two neighboring segments is also described by equation (II-20), in which $\varepsilon(d)$ is the potential energy and d the distance between the two interacting segments. However, in order to predict the properties of a polymeric liquid accurately, a third parameter c/q, together with ε^* and d^*, is necessary to characterize the random configurations of chain-like polymeric molecules in a liquid.

The law of corresponding states of polymeric liquid was made possible by Prigogine by introducing the concept of "intermolecular degrees of freedom." The cohesive energy is proportional to $Z\varepsilon^*$ (Z is the coordination number of the molecule) for a monomeric molecule, but to $qZ\varepsilon^*$ for a polymeric molecule where qZ is the number of external contacts made by the r-segments of a polymer chain. q should be less than r because some of the possible external contacts of the segments are used up by covalent bonding within the chain. For a lattice model:

$$qz = r(Z - 2) + 2 \tag{II-22}$$

and q is approximately equal to r if the lattice coordination number is 10 or greater. The expansion of the liquid plays a very important role in the theory. It is caused by the thermal vibrations of the molecules acting against the cohesive energies. However, not all thermal vibrations have an effect on expansion. Only the external degrees of freedom of movement of the molecule as a whole count. If segments within a polymer chain can rotate freely about bonds between segments, the total number of external degrees of freedom of the molecule, expressed as 3c, are:

$$3c = r + 3 \ (r \geq 2) \tag{II-23}$$

In other words, the addition of each successive segment to a dimer increases the external degrees of freedom of the molecule by one. If the polymer chain is completely rigid, then $3c = 5$, and the number of external degrees of freedom of the molecule is independent of r. Therefore, c depends on the flexibility of the polymer chain and can be considered as the "effective number of segments" if each segment were to have three external degrees of freedom like a monomeric molecule. Formally, what appears in the theory is not c, r, or q alone, but ratios like c/q or c/r, which are the number of external degrees of freedom per unit length or polymer chain (and which are taken as a measure of chain flexibility).

At least three molecular parameters now characterize a polymeric liquid: d^* and ε^* dealing with individual segments, and the so-called "structural factor" c/q (approximately equal to c/r) which has to do with the whole molecule. The structural factor was introduced by Prigogine into the characteristic temperature T^* and pressure P^* of polymeric liquids by equation (II-24):

$$T^* = \frac{\varepsilon^*}{(c/q)k}$$

$$P^* = \frac{\varepsilon^*}{(r/q)d^{*3}} \tag{II-24}$$

Prigogine and coworkers went one step further in applying corresponding states theory to polymer mixtures by assuming the same universal potential function (equation (II-20)) to characterize all like-like and like-unlike contacts. A polymer mixture can then be treated as a "pseudopure" liquid characterized by some kind of average characteristic temperature <T*> and pressure <P*>. One can then predict thermodynamic properties of the mixture providing the corresponding properties of both solute and solvent are known. This can be done by first introducing the "surface fractions" of component 1 (solvent) and component 2 (solute):

$$X_1 = \frac{q_1\ x_1}{q_1\ x_1 + q_2\ x_2}\ ;\quad X_2 = \frac{q_2\ x_2}{q_1\ x_1 + q_2\ x_2} \qquad \text{(II-25)}$$

The average <c/q> for the mixture is then defined as:

$$\langle c/q \rangle = X_1 \frac{c_1}{q_1} + X_2 \frac{c_2}{q_2} \qquad \text{(II-26)}$$

Similarly, the average potential energy <ε*> and average distance <d*> between two neighboring segments for the "pseudopure" liquid can also be evaluated, and the average characteristic temperature and pressure of the mixture are expressed by:

$$\langle T^* \rangle = \frac{\langle \varepsilon^* \rangle}{\langle c/q \rangle\ k}\ ;\quad \langle P^* \rangle = \frac{\langle \varepsilon^* \rangle}{\langle r/q \rangle \langle d^* \rangle^3} \qquad \text{(II-27)}$$

Thermodynamic properties of the mixture can then be expressed in the same form as those of pure liquids.

The corresponding states theory predicts [2A-6, 8] that the interaction parameter χ_1 in equation (II-10) can be expressed by:

$$\chi_1 = -(U/R\,T)\,\nu^2 + (C_p/2R)\,\tau^2 \qquad \text{(II-28)}$$

Here -U is the energy of vaporization of solvent, C_p is the configurational heat capacity of the solvent:

$$C_p = C_{p,\,\mathrm{liq.}} - C_{p,\,\mathrm{gas}} + R \qquad \text{(II-29)}$$

where R is the gas constant and ν and τ are defined by:

$$\tau = 1 - (T^*_2/T^*_1) \qquad \text{(II-30)}$$

$$\nu^2 = (\bar{\delta}^2/4 + 9\,\bar{\rho}^2) \qquad \text{(II-31)}$$

$\bar{\delta}$ and $\bar{\rho}$ are cohesive energy and size difference parameters, and they are defined by:

$$\bar{\delta} = (\varepsilon^*_2/\varepsilon^*_1) - 1 \qquad \text{(II-32)}$$

$$\bar{\rho} = (d^*_2/d^*_1) - 1 \qquad \text{(II-33)}$$

Thus the enthalpic and entropic contributions to the χ_1 parameter are found to be:

$$\chi_H = k_1 = ((-U + T\,C_p)/R\,T)\,\nu^2 - T/2R\,\frac{d\,C_p}{d\,T}\,\tau^2 \qquad \text{(II-34)}$$

$$\chi_S = 0.5 - \Psi_1$$

$$= - (C_p/R)\ \nu^2 + \left(\left[C_p + T\,\frac{dC_p}{dT}\right]/2\ R\right)\ \tau^2 \qquad \text{(II-35)}$$

Inspecting these equations one can see that the noncombinatorial excess properties are caused by the following two effects:

(1) Energetic effect: This effect is due to the cohesive energy and size difference between solvent molecule and polymer segment. This kind of effect is exactly the same as in monomeric mixtures.

(2) Structural effect: This effect is found to play a very important role in polymer mixtures and is directly related to the structure and chemical nature of the molecules. This effect is specific to polymeric mixtures and it is caused by the significant difference of size or chain length between polymer and solvent. As pointed out by Prigogine [2A-7], the structural effect depends primarily on the configurational specific heat and its derivative with respect to temperature. This explains clearly why, in a rigid lattice approach like that used in the simplified lattice model, the structural effect vanishes.

The recognition of the structural effect on thermodynamic properties of polymer mixtures has proved to be the key to the success of the corresponding states theory. Many important observations of polymer solution thermodynamics can be explained very well based on such structural arguments [2A-6, 7, 8, 9]. The corresponding states theory is more rigorous than other theories since it allows volume change during mixing process. The theory also gives the temperature and pressure dependence of the interaction parameter χ_1 [2A-9], and predicts a concentration dependence for χ_1 which is completely ignored by the Flory-Huggins Theory.

The corresponding states theory seems to explain some thermodynamic behavior of polymeric liquids/mixtures very well. However, the application of the theory is somewhat limited to qualitative interpretation of experimental results due to, probably, the difficulty of determining the molecular parameters d^*, ε^*, and c/q. The theory is found to be most useful in predicting thermodynamic properties of oligomer series when the three molecular parameters are known for a reference liquid [2A-10].

3. Solubility Parameter Theory

Solubility parameter theory [2A-11a], like the Flory-Huggins Theory, originated from the concept of regular solutions. According to the theory, the polymer (2) - solvent (1) interaction parameter χ_1 of equation (II-10) is related to the so-called "solubility parameters," δ, of the two components through:

$$\chi_1 = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 + \beta \tag{II-36}$$

where δ_i is defined as the square root of the "cohesive energy density" of component i:

$$\delta_i = \left(\frac{\Delta E^v}{V}\right)_i^{1/2} \tag{II-37}$$

Here ΔE_i^v and V_i are the molar energy of vaporization and molar volume of component i. The quantity β is an empirical constant found necessary for systems in which the difference in size and/or shape between solute and solvent is radical [2A-11b]. β was found to have a value of approximately 0.34 for polymer-solvent systems [2A-12].

Similar to the treatments in the Flory-Huggins Theory, the parameter χ_1 can be split into enthalpic and entropic contributions, i.e., χ_H and χ_S , where:

$$\chi_H = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \tag{II-38}$$

$$\chi_S = \beta \tag{II-39}$$

The parameter χ_H is related to the heat of mixing of the polymer with the solvent. The use of equation (II-38) allows only positive values for χ_H. Thus the theory predicts that a polymer is soluble in a solvent when the solubility parameters of the two components have nearly the same value. This approach for selecting good solvents for a particular polymer has proved to be very successful. However, exceptions were observed in some cases. Later refinements of the theory [2A-12, 13] suggested the usefulness of separating the cohesive energy densities into non-polar, polar and hydrogen bonding parts, i.e.,

$$\delta_i^2 = \delta_{i,\ np}^2 + \delta_{i,\ P}^2 + \delta_{i,\ H}^2 \tag{II-40}$$

A more general expression for χ_H can then be written as:

$$\chi_H = \frac{V_1}{RT} [(\delta_{1,\ np} - \delta_{2,\ np})^2 + (\delta_{1,\ P} - \delta_{2,\ P})^2 + (\delta_{1,\ H} - \delta_{2,\ H})^2] \tag{II-41}$$

All three contributions to the solubility parameters for most solvents and commercial polymers can easily be found in the literature [2A-14].

The parameter χ_S was originally introduced to correct the supposed inadequacy of the Flory combinatorial entropy approximateion. According to the original derivation [2A-16]:

$$\chi_S = \frac{1}{Z} \tag{II-42}$$

where Z is the coordination number of the quasi-lattice model and is expected to have a value between 10 and 12. The difference between 0.34 and 1/Z is explained by Guggenhaim [2A-15] to be due to the excluded-volume effect. The difference might also be explained as the result of the structural effects discussed in the corresponding states theory.

Although the solubility parameter theory is based on the assumption that the volume change in mixing process is negligible, Patterson [2A-16, 17] argued that the theory can also take into account the effects of the volume change of mixing. According to Patterson and co-workers, the simple solubility parameter theory has great similarity to the more rigorous corresponding states theory, and predicts many of the important observations of polymer solution thermodynamics as well. The comparison given by Patterson between the solubility parameter theory and the corresponding states theory provides a strong theoretical basis for the solubility parameter theory.

Besides the theoretical background, the solubility parameter theory overcomes the serious defect of the Flory-Huggins Theory that the interaction parameter χ_1 cannot be predicted or calculated from basic data for the pure components, but must be determined experimentally. It seems likely that solubility parameter theory will continue to be widely applied, particularly in the polymer industry, for the foreseeable future.

4. Excluded Volume Theory

Excluded volume theory takes a completely different approach from the other three theories to explain the thermodynamic properties of polymer solutions. The theory says that if one can predict the average dimensions of polymer molecules in an infinitely dilute solution, it should be possible to determine the thermodynamic properties of the solution because both are affected by interactions between solvent and polymer segments in the solution.

Consider a polymer molecule in an infinite solvent medium. The dimension of the polymer molecule (either the mean-square end-to-end distance $<R^2>$ or the mean-square radius of gyration $<S^2>$) is determined by the position of each successive segment in the solution. As one would expect, the direction of a given segment, for example the jth segment, is strongly affected by the direction of its predecessor (i.e., the (j-1)th segment) due to bond angle restrictions. It is also influenced to some extent by the directions of other neighbors (the(j-2)th, etc.) due to hindered rotations. It is reasonable to assume that one bond has no appreciable influence upon the rotation of another bond when they are far apart. Thus, such interactions between bonds are referred to as "short-range interference." However, two or more segments remote from one another along the chain cannot occupy the same volume at the same time because of their finite volume. In other words, repulsive forces will act between these segments when close to one another. This repulsive force will be altered by the existence of solvent molecules and be affected by the temperature of the solution. Interactions of this sort are usually referred to as the "excluded-volume effect" and are of long-range nature. It is quite obvious that two types of excluded volume can be distinguished: the intramolecular and intermolecular excluded volumes. The polymer chain with only short-range interferences is called the ideal or unperturbed chain, and its molecular dimension is called the unperturbed dimension. The term "unperturbed" indicates there is no excluded volume effect.

According to excluded volume theory, the average polymer molecular dimension and thermodynamic properties such as osmotic virial coefficients may be expressed in terms of two basic parameters. One is the unperturbed mean-square end-to-end distance $\langle R^2 \rangle_0$, and the other is the excluded-volume parameter, usually designated by z. The quantity z is proportional to the effective excluded volume for a pair of chain segments at infinite dilution and also to the square root of the number of segments in the chain n, i.e.:

$$z = \left(\frac{3}{2 \Pi n \bar{a}^2}\right)^{3/2} \beta n^2 \qquad \text{(II-43)}$$

$$= \left(\frac{3}{2 \Pi \langle R^2 \rangle_0}\right)^{3/2} \beta n^2$$

where $\bar{a}$ is the effective bond length and β is the "binary cluster integral" for a pair of segments. It represents the effective volume excluded to one segment by the presence of another. Generally, β will have large positive values in good-solvent systems (where preferential attractions occur between the polymer segment and solvent molecule) and small negative values in poor-solvent systems.

The conclusion of the theory can be summarized by expressions for the molecular dimension and for the osmotic second virial coefficient, A_2.

$$\alpha_R^2 = 1 + \frac{4}{3} z - 2.075 z^2 + 6.459 z^2 - --- \qquad \text{(II-44)}$$

$$\alpha_S^2 = 1 + 1.276 z - 2.082 z^2 + --- \qquad \text{(II-45)}$$

where, α_R^2 and α_S^2 are defined by the expressions:

$$\alpha_R^2 = \langle R^2 \rangle / \langle R^2 \rangle_0 . \qquad \text{(II-46)}$$

$$\alpha_S^2 = \langle S^2 \rangle / \langle S^2 \rangle_0 . \qquad \text{(II-47)}$$

and

$$A_2 = (N_A n^2 \beta / 2 M^2) h(z) \qquad \text{(II-48)}$$

He

gi

o

t

d

d

Here, N_A is the Avagadro constant and the function h(z) is given [2A-18] by:

$$h(z) = 1 - 2.865\ z + 14.278\ z^2 - \cdots \qquad \text{(II-49)}$$

Equations (II-44) to (II-49) represent the exact theory of the excluded-volume effect within the framework of the two-parameter theory. Since the quantity $(N_A\ n^2\ \beta/2\ M^2)$ is independent of polymer molecule weight M, and h(z) is a decreasing function of M, the excluded volume theory predicts that A_2 decreases very slowly with increasing polymer molecular weight. Furthermore, equations (II-44) and (II-45) predict that $A_2 = 0$ and $h(z) = 1$ at the theta temperature (β and z vanish).

The excluded volume theory seems to be able to provide a correct description of the qualitative aspects of solution properties insofar as it is concerned with very dilute solutions of flexible-chain polymers. However, as pointed out by Yamakawa [2A-18], the theory breaks down for stiff chains and for concentrated solutions. In addition, the theory is expected to be valid only for $|z| \leq 0.15$, i.e., the very vicinity of the theta condition, since the series h(z) of equation (II-49) converges very slowly. All of these restrictions, along with the fact that the theory is unable to predict solution properties without prior knowledge of the two parameters $n^2\beta$ and $n\bar{a}^2$ (which can only be obtained experimentally) make the theory less attractive than solubility parameter theory.

B. Diffusion in Polymer Solutions

The characteristics of polymer solutions change greatly over large concentration range. At the infinitely dilute extreme, the polymer molecules are widely dispersed in the solvent, and there are no interactions between individual polymer chains. As the polymer concentration is increased, polymer molecules interact hydrodynamically with each other even though the domains of individual polymer molecules do not yet overlap. This concentration range is traditionally referred to as the dilute solution region. As the polymer concentration is further increased, the domains of the polymer molecules begin to overlap, there is a considerable amount of polymer-polymer contact, and entanglements are formed between polymer chains. Such solutions are referred to as "concentrated" even though in terms of molar concentration, they might be quite dilute.

Although the rate of diffusion of polymer molecules in solution has long been of considerable empirical and theoretical interest, present understanding of diffusion in polymer solutions is still far from satisfactory. There exists no general theory which is capable of describing the complete range of the complex diffusion behavior exhibited by polymer-solvent mixtures. Until recently, reasonable estimates of diffusion coefficients were possible only for self-diffusion and for infinitely dilute binary solutions, and methods for predicting the concentration dependence of diffusion rates were available only for dilute, non-electrolyte, non-associating polymer solutions. This situation results in large part from the lack of a usable kinetic theory of polymer solutions and from the lack of reliable experimental data.

In the following discussion, diffusional properties in infinitely dilute and dilute polymer solutions will be considered. First, various theories for predicting diffusion coefficients at infinite dilution are presented, and second, the theoretical approach of Vrentas and Duda to describe this concentration dependence of binary diffusion coefficients in the dilute concentration region is reviewed.

1. Diffusion in Infinitely Dilute Polymer Solutions

a. The Kirkwood-Riseman Theory

The Kirkwood-Riseman Theory [2B-1] of transport processes provides a general description of frictional properties of dilute solutions of flexible polymer molecules. The frictional properties of dilute polymer solutions are different from those of small molecule solutions, in that for each solute molecule there are a large number of "centers of resistance" to the flow of the solvent medium instead of just one. "Hydrodynamic interaction" always occurs between the resistance centers. According to the theory, the hydrodynamic interactions between segments cause velocity perturbations in the fluid and therefore affect the frictional and diffusion coefficients of polymer molecules in solution. Based on this concept, Kirkwood and Riseman derived the following equation for the translational diffusional coefficient in infinite dilution:

$$D^0 = \frac{kT}{n\zeta}\left(1 + \frac{8}{3} X\right) \qquad \text{(II-50)}$$

where

$$X = \frac{(2n)^{\frac{1}{2}}\, \zeta}{(12\, \Pi^3)^{\frac{1}{2}}\, \eta_0\, \bar{a}} \qquad \text{(II-51)}$$

Here, D^0 is the diffusion coefficient at infinite dilution, n is the number of segments in a chain, $\bar{a}$ is the effective bond length, and η_0 the solvent viscosity. The quantity ζ is the frictional coefficient of a segment and is dependent on the fluid medium and the structure of the segment unit. Equations (II-50) and (II-51) are derived based on the assumption of a random flight (unperturbed) polymer chain, and therefore are valid only for infinitely dilute solutions at the theta condition. The parameter X is a measure of the hydrodynamic interactions between segments. When $X=0$, there is no hydrodynamic interaction, and this is referred to as the "free-draining" case. In the free-draining case (or when the molecule is small, i.e., n is small), polymer molecules behave hydrodynamically as rigid spheres, and the theory predicts that D^0 is inversely proportional to polymer molecular weight. The other limiting case ($X=\infty$) corresponds to very large hydrodynamic interactions between segments, and is referred to as the "non-free-draining" case. For non-free-draining polymer-solvent systems, equation (II-50) can be reduced to:

$$(D^0)_\theta = \frac{8kT}{3n\zeta} X \qquad \text{(II-50')}$$

The subscript θ indicates equation (II-50') applies for theta solutions only. Substituting equation (II-51) into equation (II-50') gives:

$$(D^0)_\theta = \frac{0.196\, kT}{\eta_0\, n^{\frac{1}{2}}\, \bar{a}} = \frac{0.196\, kT}{\eta_0 \langle R^2 \rangle_0^{\frac{1}{2}}} \qquad \text{(II-52)}$$

where $\langle R^2 \rangle_0$ is the mean square end-to-end distance of the unperturbed polymer chain. The theory predicts that for the non-free-draining case D^0 is inversely proportional to the square root of polymer molecular weight, but is independent of the frictional coefficient (ζ). For non-theta solutions, Raju [2B-2] has suggested that a correction factor (2-2γ) be multiplied to the right hand side of equation (II-52) for the diffusion coefficient at infinite dilution.

$$D^0 = \frac{0.196\ kT}{\eta_0 \langle R^2 \rangle_0^{\frac{1}{2}}} (2 - 2\gamma) \qquad \text{(II-53)}$$

where the parameter γ is defined by the relation:

$$[\eta] = K_v \overline{M}_v^{\gamma} \qquad \text{(II-54)}$$

Here $[\eta]$ is the intrinsic viscosity of the solution and $\overline{M}_v$ is the viscosity average polymer molecular weight. In general, γ varies from 0.5 for a theta solvent to 0.8 for a good solvent [2B-3]. Thus (2-2γ) represents a small correction for the so-called "excluded-volume effect" of polymer solutions. Raju's D^0 data for styrene-acrylonitrile copolymer solutions [2B-2] are in agreement with equation (II-53).

b. Flory's Theory

The principle behind Flory's theory of transport properties of polymer molecules in infinitely dilute solutions [2B-4] is similar to that of the Kirkwood-Riseman Theory in that both assume a relative velocity (i.e., the velocity of the solvent with reference to the molecule) gradient along the radius of the molecule. This is illustrated in Figure 1. The "depth of penetration" of the molecule by the flow should be dependent on the structure of the polymer segment, the size and shape of the polymer molecule in solution, and, according to Flory, can be characterized by the variable ζ/η_0. The parameter ζ/η_0 can be considered as the "effective size" of one segment since it increases with polymer molecular weight provided $<R^2>^{\frac{1}{2}}$ remains constant. Thus, the lower the ratio ζ/η_0, the closer the solvent flow will penetrate to the molecular center, leading to the free-draining case. Flory argued if the ratio ζ/η_0 is great enough such that the solvent flow is excluded from the inner more densely populated regions of the molecule (which is believed to be the case for polymer solution) a condition of comparative insensitivity of the flow pattern ζ/η_0 should be approached. Flory then concluded that the frictional coefficient f^0 of the molecule as a whole (at fixed η_0) should be independent of the frictional coefficient ζ of a segment in the limit of sufficiently large ζ/η_0. Based on the above discussion, Flory suggested that the molecular frictional coefficient should depend only on the size $<R^2>^{\frac{1}{2}}$ and not otherwise on the nature of the polymer if the molecular weight is sufficiently large. That is:

$$f^0/\eta_0 = P<R^2>^{\frac{1}{2}} \tag{II-55}$$

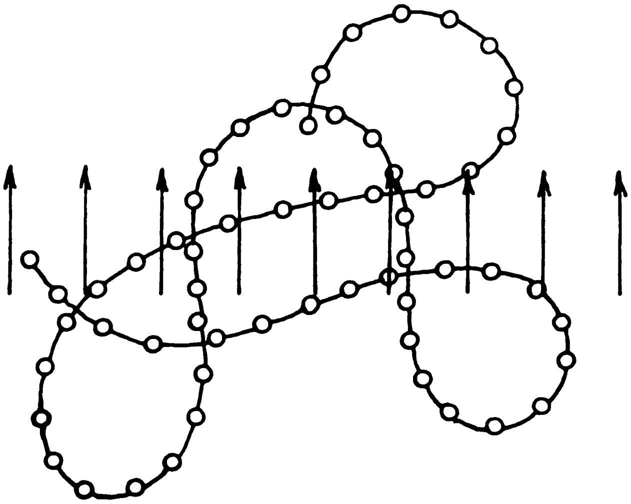


Figure 1A. A Free-Draining Molecule During Translation Through Solvent.*

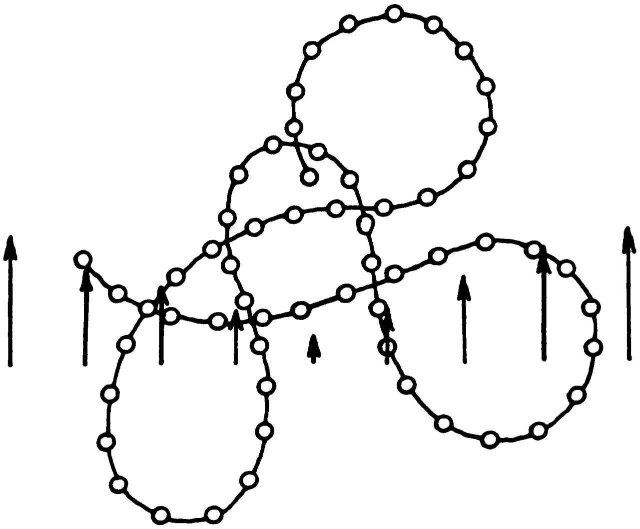


Figure 1B. Translation of a Chain Molecule with Perturbation of Solvent Flow Relative to the Molecule.*

---

*Arrows indicate flow vectors of the solvent relative to polymer chain.

where P is a universal constant. A random flight model was used to show that P should have a value of 5.11.

Using similar arguments, Flory also proposed that the intrinsic viscosity $[\eta]$ depends primarily on the ratio $\langle R^2\rangle^{3/2}/M$, consisting of a volume divided by the molecular weight:

$$[\eta] = \Phi \langle R^2\rangle^{3/2}/M \tag{II-56}$$

where Φ is another universal constant and has a theoretical value of 3.62×10^{21}. However, experimental results show that Φ is approximately equal to 2.5×10^{21}.

Combining equations (II-55) and (II-56), one gets:

$$f^0 = \frac{P\,\Phi^{-1/3}\,\eta_0}{(M[\eta])^{-1/3}} \tag{II-57}$$

Thus,

$$D^0 = \frac{kT}{f^0} = \frac{kT(P^{-1}\,\Phi^{1/3})}{\eta_0\,(M[\eta])^{1/3}} \tag{II-58}$$

According to equation (II-57), the molecular frictional coefficient f^0 should vary with M to the 0.5 power in a theta solvent, and slightly greater than 0.5 (but never greater than 0.6) in a good solvent. Flory has suggested that f^0 is related to the molecular weight by:

$$f^0 = K_f\,M^{(\frac{1}{2} + a')} \tag{II-59}$$

where K_f is a constant, and a' is given by:

$$a' = (\gamma - \tfrac{1}{2})/3 \qquad \text{(II-60)}$$

The parameter γ is defined by equation (II-54). Therefore, the theory predicts that D^0 should vary inversely with M to a power between 0.5 and 0.6. Equation (II-58) allows one to estimate the value of D^0 provided the viscosity of the solvent η_0, the polymer molecular weight M and the intrinsic viscosity $[\eta]$ of the system are known.

c. Johnston's Theory

Recently Johnston and Rudin [2B-5] derived a simple expression for the diffusion coefficient of an infinitely dilute polymer solution. By combining the well known Einstein equation for the concentration dependence of solution viscosity [2B-6], with the Mark-Houwink equation (equation (II-54)), the mean radius of pseudo-spherical polymer molecules in solution, R_e, can be related to the viscosity average molecular weight $\overline{M}_v$ by the expression:

$$K_v \, \overline{M}_v^{1+\gamma} = (10 \, \Pi \, N_A/3) \, R_e^3 \qquad \text{(II-61)}$$

where R_e is defined by the relation

$$\underline{V} = \frac{4}{3} \, \Pi \, R_e^3 \qquad \text{(II-62)}$$

Here, $\underline{V}$ is the mean volume occupied by a single polymer molecule in solution. Johnston went one step further by assuming that R_e is the same as the equivalent hydrodynamic radius of a non-free-draining pseudo-spherical polymer

P

Th

be

an

ex

Eq

(I

co

Ac

p

as

Fl

a

Jo

ti

Ce

particle, R_e, defined by the equation:

$$f^0 = 6 \Pi \eta_0 R_f \qquad \text{(II-63)}$$

The frictional coefficient at infinite dilution f^0 can then be rewritten as:

$$f^0 = 6 \Pi \eta_0 \left(\frac{10 \Pi N_A}{3 K_v \bar{M}_v^{1+\gamma}}\right)^{-1/3} \qquad \text{(II-64)}$$

and the diffusion coefficient at infinite dilution D^0 is expressed by:

$$D^0 = \frac{kT}{6 \Pi \eta_0} \left(\frac{10 \Pi N_A}{3 K_v \bar{M}_v^{1+\gamma}}\right)^{1/3} \qquad \text{(II-65)}$$

Equation (II-65) is in exactly the same form as equation (II-58) of Flory's theory, and the corresponding universal constant $P^{-1}\Phi^{1/3}$ in equation (II-58) can be expressed as:

$$P^{-1}\Phi^{1/3} = \frac{1}{6} \left(\frac{10 \Pi N_A}{3}\right)^{1/3} \qquad \text{(II-66)}$$

According to equation (II-66), the universal constant $P^{-1}\Phi^{1/3}$ has a value of 9.80×10^6 which is about three times as high as the theoretical value 3.39×10^6 predicted by the Flory theory. The difference between the two theories might arise from Johnston's assumption that $R_e = R_f$. However, Johnston showed that D^0 values evaluated according to equation (II-65) agree with experimental values within ten percent for over 40 polymer-solvent systems.

d. Fedors' Empirical Relation

Recently, Fedors proposed the following empirical relationship for the estimation of the self-diffusion coefficient of pure liquids [2B-7]:

$$D_{11} = \frac{4.5 \times 10^{-9} \, (V^* - V) \, T}{\eta_0 \, V^{*\,4/3}} \qquad \text{(II-67)}$$

where D_{11} is the self-diffusion coefficient in units of $cm^2/sec.$, V^* and V are the molar volumes of the liquid at the critical temperature and temperature T(°K), respectively, and η_0 is the viscosity of the liquid at temperature T expressed in Poises. The correlation constant 4.5×10^{-9} and the exponent 4/3 in equation (II-67) were determined by Fedors by correlating data taken from the literature. The relationship is found to be valid not only for small molecular liquids, but also for high molecular weight polymeric liquids. Fedors suggested that critical molar volumes for polymeric liquids (which are generally not measurable) can be calculated using a group contribution method which he described [2B-8].

He also proposed that the limiting diffusion coefficient of an infinitely dilute solute (D^0) can be related to the self-diffusion coefficient of the solvent D_{11} by the symmetrical relationship [2B-9, 10].

$$D^0 \, (V_2^* - \overline{V}_2^0)^{\frac{1}{2}} = D_{11} \, (V_1^* - V_1)^{\frac{1}{2}} \qquad \text{(II-68)}$$

Here, V_2^* and V_1^* are the molar volumes at the critical temperatures for the solute and solvent, respectively, $\overline{V}_2^0$ is the partial molar volume of the solute in infinitely dilute solution, and V_1 is the molar volume of the solvent. Fedors mentioned that equation (II-68) is suitable for both liquid-liquid and gas-liquid systems.

Combining equation (II-68) with equation (II-67), one gets:

$$D^0 = \frac{4.5 \times 10^{-9} \ (V_1^{*} - V_1)^{3/2} \ T}{\eta_0 \ V_1^{*\,4/3} \ (V_2^{*} - \overline{V}_2^0)^{1/2}} \qquad \text{(II-69)}$$

from which the diffusion coefficient at infinite dilution can be estimated directly, given η_0, V_1 and $\overline{V}_2^0$. Equation (II-69) was tested by Fedors for some 52 solutes in eight different solvents. The average percent error was found to be 22.3 percent. The most serious errors occur in those systems in which one or both of the components associate to form moltimers. The simple expression of equation (II-69) seems to offer a reasonable correlation between the limiting diffusion coefficient D^0 and properties of pure solute and solvent.

2. Diffusion in Dilute Polymer Solutions

Most diffusion data in the literature indicate that the diffusion rate of a polymer in solution varies linearly with concentration in the dilute region. In general, diffusivities are found to increase with increasing polymer concentration, although there are some systems which show the opposite behavior. These later systems are of special interest in this work, and are considered in detail later. Whichever the case, the diffusion coefficient for dilute polymer solutions can conveniently be expressed by a series expansion of the following form:

$$D = D^0 \ (1 + k_d \, \rho_p + \text{---}) \qquad \text{(II-70)}$$

where ρ_p is the polymer mass concentration. Thus the diffusion coefficient for dilute solutions can be predicted from a knowledge of the parameters D^0 and k_d.

Recently Vrentas and Duda [2B-11] showed that the parameter k_d can be predicted using the equation:

$$k_d = 2 \, A_2 \, \overline{M}_N - k_s - b_1 - 2 \, \overline{V}_2^0 \qquad \text{(II-71)}$$

Here A_2 is the osmotic second virial coefficient, $\overline{M}_N$ is the number average molecular weight of polymer, and $\overline{V}_2^0$ is the partial specific volume of the infinitely dilute polymer. The quantities b_1 and k_s are defined by series expansions for the concentration dependence of the partial specific volume of the solvent ($\overline{V}_1$) and the frictional coefficient of the polymer.

$$\overline{V}_1 = \overline{V}_1^0 \ (1 + b_1 \ \rho_p + ---) \qquad \text{(II-72)}$$

$$f = f^0 \ (1 + k_s \ \rho_p + ---) \qquad \text{(II-73)}$$

k_s accounts for the effects of intermolecular hydrodynamic interactions on the frictional properties of polymer molecules in solutions.

According to equation (II-71), k_d includes three contributing effects: (1) the thermodynamic term $2A_2\overline{M}_N$; (2) the hydrodynamic term k_s; and (3) volumetric effects b_1 and $2\overline{V}_2^0$. Volumetric effects generally are insignificant but become important when k_d is small. When the thermodynamic effect dominates the hydrodynamic effect, k_d is positive and the diffusion rate increases with concentration. On the other hand, the diffusion rate decreases with concentration if the hydrodynamic effect becomes dominant. It should be pointed out that equation (II-70) is valid only for non-electrolyte, non-associating polymer-solvent systems because the concentration dependence of the diffusion coefficient of electrolyte and/or associating polymer solutions is, in general, nonlinear even within the dilute region.

III. EXPERIMENTAL METHOD FOR MEASURING OSMOTIC PRESSURES OF DILUTE POLYMER SOLUTIONS

A. Experimental Apparatus and Principle of Operations

Measurement of osmotic pressures in determination of number average molecular weights has not been used extensively in the past because of the time-consuming nature of the classical method and the attendant errors caused by the lengthy observation period. Bruss and Stross [3A-1] have discussed some of the dynamic methods described in the literature [3A-2, 3, 4] with attention to the errors caused by solute permeation of the membrane and the importance of completing the measurement as rapidly as possible.

A Hallikainen automatic membrane asmometer (Model 1361 - Code D, designed by Shell Development Co.) was used in this work to measure osmotic pressures of polymer solutions. The instrument needs only 10 cc sample solution, which is then isolated in the osmometer cell using the inlet and outlet valves. After a period of about 6 to 20 minutes, depending upon the permeability of the membrane, the osmotic pressure is observed on a Veeder-Root type counter which reads osmotic pressure head of the solvent used. A built-in recorder, the pen of which is directly driven by a balancing servo, enables the operator to follow the servo balancing of osmotic pressure and degree of membrane permeation, if any.

Figure 2 is a schematic diagram of the sample flow scheme. The osmometer cell consists of two cavities separated by a semipermeable membrane. The sample cavity includes a thin metal diaphragm which is responsive to volume changes and has suitable valves to admit and isolate a sample. The solvent cavity is connected to a servo-driven plummet in a vertical tube of solvent. The plummet is capable of changing the solvent head, thus causing solvent to flow through the membrane in either direction depending upon the differential pressure. Displacement of the metal diaphragm caused by flow through the membrane is sensed as a capacitance change of an oscillator circuit, causing a servo to null the solvent head for zero osmotic flow. At null balance the servo comes to rest with the solvent meniscus depressed by the amount of the osmotic pressure. The mechanical counter geared to the plummet servo registers this depression and hence the osmotic pressure. The recorder shows the entire balancing cycle and (by the slope of the curve following the maximum indicated osmotic pressure) the degree of solute permeation through the membrane. A more detailed description of the experimental procedure is given by Rolfson and Coll [3A-5].

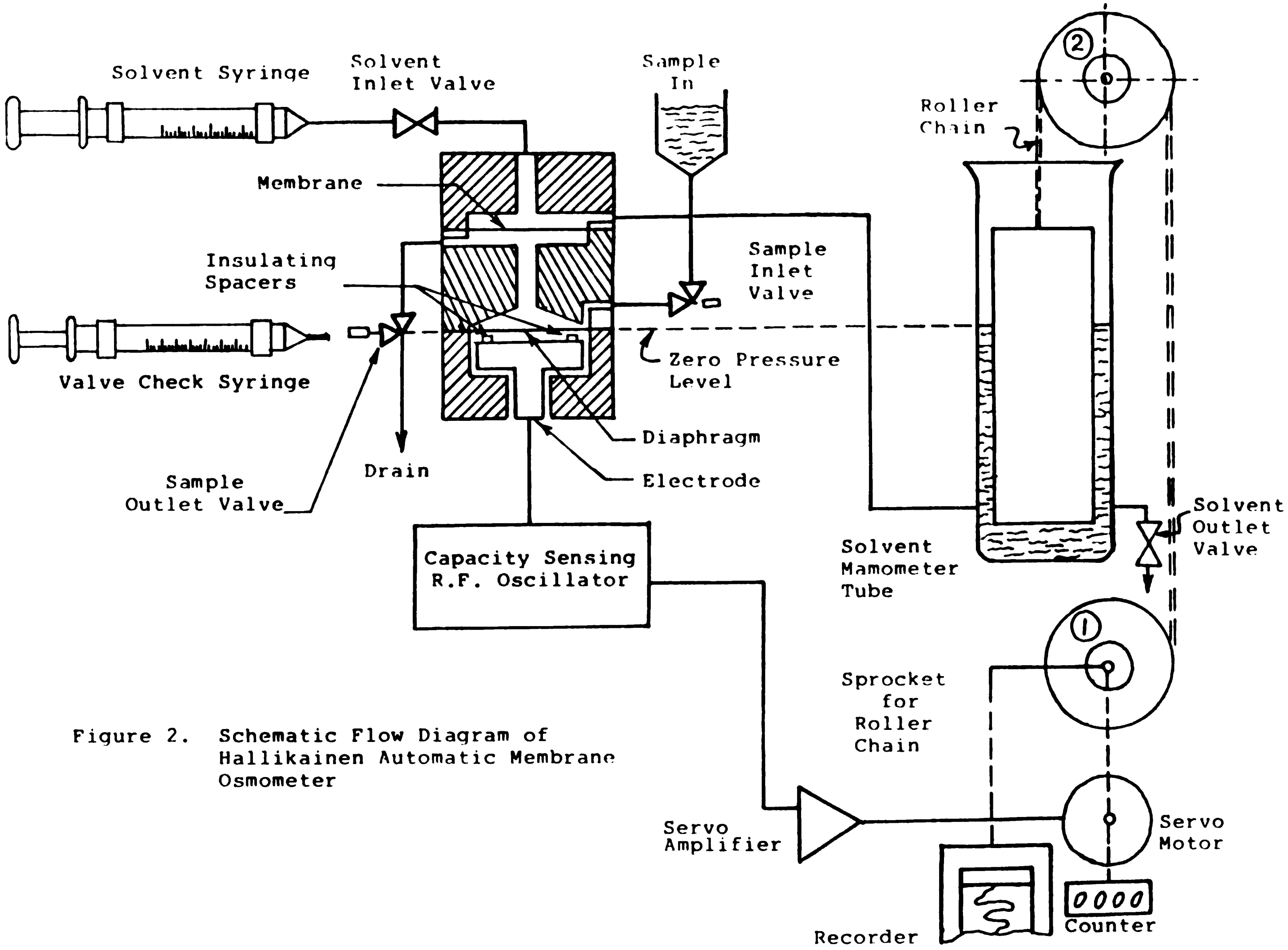


Figure 2. Schematic Flow Diagram of Hallikainen Automatic Membrane Osmometer

B. Membrane Conditioning

An important factor in osmotic pressure measurements is the careful conditioning of the membrane to the particular solvent employed. Membrane materials of the greatest interest to the polymer chemist and other research workers concerned with osmotic pressure measurements are the swellable organo-colloid materials. Membranes made of these materials swell to a different extent in each solvent. Thus, the permeability of a membrane will vary with the solvent.

The membranes are generally packed with a solution which prevents bacterial growth. This solution must be removed from the membranes. When aqueous solutions are to be employed, the membranes should be rinsed under running water and then laid for sixty minutes in distilled water before use. If the solvent to be used is different from water the membranes must be conditioned; first for removal of all water, and second for uniform permeability to the type of solvent. The following conditioning procedures were used in this work with successful results. The membrane must be handled gently with a soft, smooth instrument or gloved hands. It must not be allowed to dry during or after conditioning.

Ethanol drying procedure. (The wash intervals indicated are the minimum recommended. Longer washes may be used without adverse effects.)

(1) Wash in distilled water for one hour

(2) Wash in 25% ethanol/water for ½ hour

(3) Wash in 50% ethanol/water for ½ hour

(4) Wash in 75% ethanol/water for ½ hour

(5) Wash in pure ethanol for ½ hour

(6) Wash in fresh, absolute alcohol for ½ hour

In order to condition a membrane to another solvent, condition in 25% increments of increasing solvent concentration. For some solvents, it has been found necessary to condition the membrane through an intermediate solvent (e.g., from ethanol, through toluene, to dimethylformamide).

<u>To condition from ethanol to a solvent</u>.

(1) Wash in 25% solvent/ethanol for ½ hour

(2) Wash in 50% solvent/ethanol for ½ hour

(3) Wash in 75% solvent/ethanol for ½ hour

(4) Wash in pure solvent for 1 hour

After conditioning, the membrane should be stored in fresh, cool solvent until ready for use.

The permeability of a membrane is better retained if it is not heated prior to use. For high temperature operation, the membrane is installed on the cell block and the temperature control is set before the main power is turned on. As the cell heats the membrane is conditioned to the new temperature.

C. Experimental Procedure

Part a: Start-Up Procedure

(1) Install the membrane.

(2) Set the desired operating temperature by adjusting the SET POINT potentiometer. The minimum operating temperature should be at least 10°C above ambient temperature for satisfactory temperature control.

(3) Turn on main power and wait about 1½ hours for thermal stabilization.

(4) Flush both solvent and sample cell with clean solvent. Make sure that any air trapped in the cells is removed.

(5) Run the manometer plummet down until the mechanical counter reads zero.

(6) Make the solvent meniscus in the manometer tube coincide with the reference position index mark by using a syringe to insert extra (or withdraw excess) solvent through the SOLVENT OUTLET.

(7) Adjust the oscillator so that the recorded pen is on the chart reference line. This will be the base line.

(8) Fill the sample funnel with the sample polymer solution. Open the OUTLET VALVE to allow the sample to flow into the sample cell, then firmly close.

(9) Turn on the heater and wait for thermal equilibrium.

(10) Close the sample INLET VALVE and immediately open sample OUTLET VALVE. The pen will move to the bottom

of the chart. Wait for a few minutes and then close the sample OUTLET VALVE. The resulting osmotic pressure is indicated by the difference between the base line reading and the new steady-state reading.

Part b: Recommended Procedure for Molecular Weight Determination.

(1) Flush sample and solvent chambers with pure solvent from the same container. All solvent used, both the pure and that mixed with the solute, should be from the same supply.

(2) Make two or three blank runs, each of 10 to 15 minutes duration, with pure solvent on both sides of the membrane. These readings will indicate the reproducibility of the base line.

(3) Make a sample solution of 0.5 grams per 100 cc of solvent. Flush the sample cell thoroughly with two funnels full of this solution.

(4) Fill sample cell with above solution and make a trial run. This will indicate the concentrations to use for the molecular weight determination and indicate the presence of solute components small enough to pass through the membrane.

(5) Flush the sample cell, and record another run with pure solvent. Check the final value with that of step (2). If this reading is below the initial base line, then there has been solute permeation into the solvent side.

(6) Make up several concentrations (using the result of step (4)) that will provide on-scale experimental points.

(7) Starting with the most dilute solution, flush the sample cell using two funnels (about 14 cm^3). Retain the last 2 cm^3 in the cell.

(8) Take a 5 to 10 minute osmotic pressure reading.

(9) Repeat steps (7) and (8) using sample solutions of increasing concentration until at least five experimental points have been determined.

(10) Check the base line before, after, and several times during operation as a means of determining reference stability. Where readings are taken over an extended period of time, evaporation of solvent as well as ambient temperature changes may cause a slight shift in the base line. Make a plot of the base line position as a function of time and use it to correct readings for which the shift has been appreciable.

D. Error Analysis

The main cause of error results from the permeation of solute molecules through the membrane. This became particularly evident when the solute molecular weight was too low. When solute permeation is detectable, extrapolation of osmotic pressure to zero time is necessary to minimize error. The relatively poor temperature control system of this instrument might also cause observable error. This was minimized by setting the controller at least 10°C higher than room temperature. The repeatability of osmotic pressure measurements in this work is found to be within ± 0.02 cm.

IV. EXPERIMENTAL METHOD FOR MEASURING DIFFUSION COEFFICIENTS OF DILUTE POLYMER SOLUTIONS

A. Experimental Apparatus

A Mach-Zehnder interferometer described by Bidlack [4A-3] was used to study binary diffusion in the polymer solutions. The technique involves forming a sharp interface between a more concentrated polymer solution with a less concentrated solution in an optical cell where diffusion occurs. The cell is immersed in a constant temperature bath, and the diffusion process is followed by measuring the rate of change of refractive index of the solution with the Mach-Zehnder [4A-1] interferometer. The two solutions of slightly different concentrations are carefully layered, one on top of the other, into the cell and free diffusion allowed to take place after a sharp interface is formed between the solutions. The diffusion coefficient obtained in this way is assumed to be that of a concentration which is the average of the two solution concentrations.

A diagram and photograph of the interferometer are shown in Figures 3 and 4. The various components of the interferometer are supported by ordinary laboratory bench carriages stationed along a continuous rail composed of

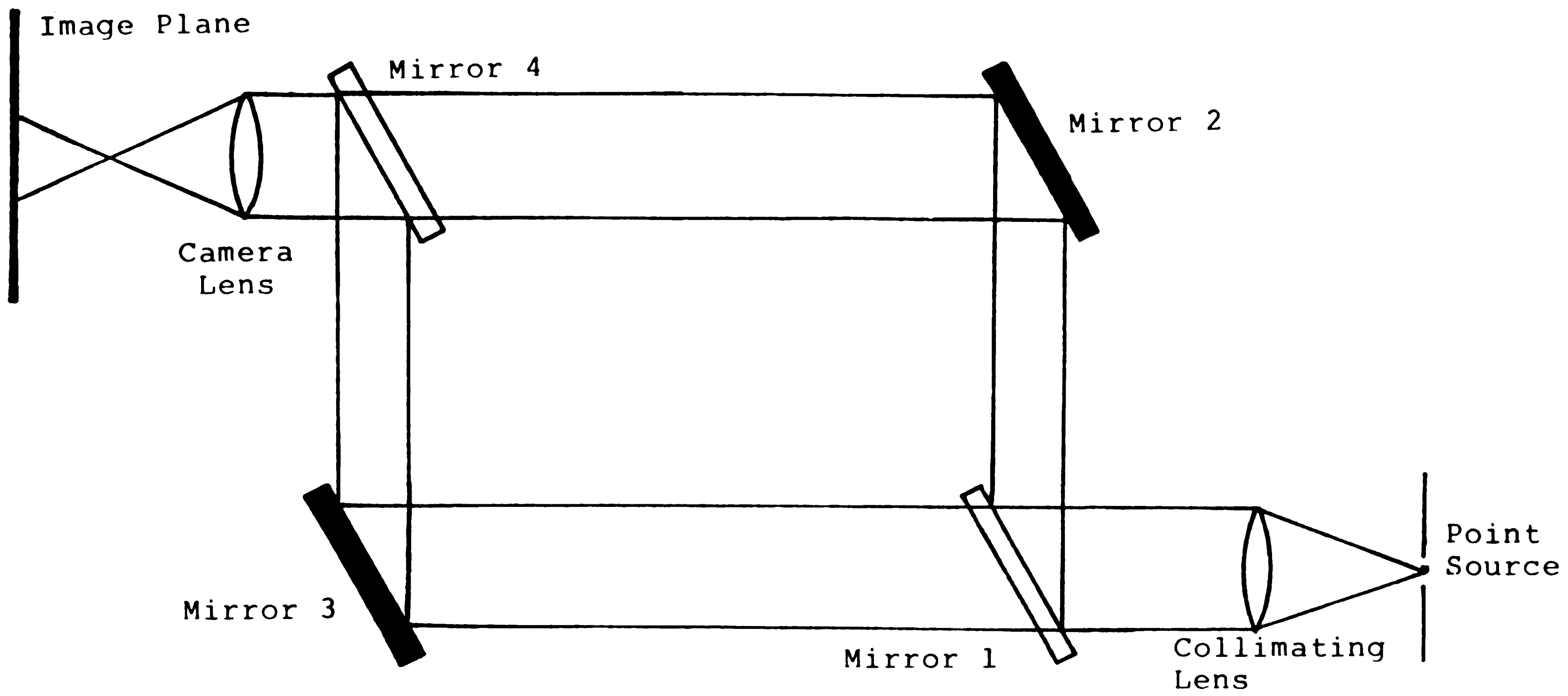


Figure 3. Schematic Diagram of Interferometer Showing Position of Mirrors

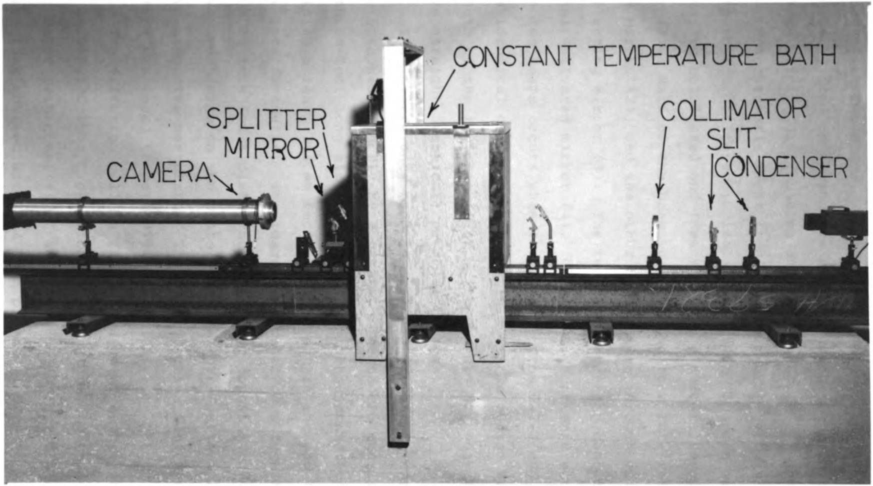


Figure 4. Photograph of Mach-Zehnder Interferometer Showing Components.

three optical benches. These in turn are bolted to an I-beam mounted on a concrete block on rubber cushions to dampen outside disturbances and vibrations.

Monochromatic light from a Cenco quartz mercury arc lamp source, filtered to isolate the 5461 °A green mercury line, is collimated and then split by a half-silvered mirror (1). Half of the beam is reflected to a full reflecting mirror (2), and the other half passes through a full reflecting mirror (3). The two beams are then combined at a half-silvered mirror (4). Constructive interference of the two beams occurs when the path lengths 1-2-4 and 1-3-4 are identical or differ by a whole multiple of the wavelength of the incident light. The mirrors are adjusted to give straight, vertical, parallel fringes.

The interference beam is arranged so that it can be photographed directly by a camera. The camera consists of a three-foot long aluminum tube (3.5 inches diameter) containing a lens (343 mm focal length) set in the end towards the interferometer. The image is focused on a type M, 3¼ × 4¼ inch Kodak plate located at the opposite end. A lever mechanism on the plate holder allows fourteen successive exposures per plate. The magnification factor of the camera was found to be 1.929.

The diffusion cell is fixed in a water bath maintained at 34.0±0.1°C by a proportional temperature controller. The water bath consists of an 18 × 18 × 18 inch stainless steel tank covered with 3/4 inch plywood and resting on the cement block without touching the interferometer. Two round optical flat windows, 3 inches in diameter, are clamped and sealed into the water bath and aligned to allow passage of the light beams through the bath and cell windows. Distilled water is used as the temperature controlling medium.

Figures 5 and 6 show a photograph and a diagram of the diffusion cell. The main body of the cell consists of a ¼ × 3¼ inch slot cut into a stainless steel plate with optical flat windows clamped over the slot to form a sealed channel. The channel is situated to allow both light beams to pass through it; thus, a vertical concentration gradient in the solution across one of the beams results in a fringe displacement pattern that is a direct plot of refractive index versus distance. All parts of the cell which are in contact with the liquid solutions are stainless steel or glass.

A frame is bolted to the cement block and positioned above the bath so the cell can be hung from the top and immersed in the bath. Two small position pins located on the frame insures that the cell is always placed in the same position.

The cell is provided with two inlets (one on the top and the other in the bottom) and two outlets directly across from each other about one-third of the way up the channel sides. The two solutions of slightly different concentrations are slowly flowed simultaneously into the

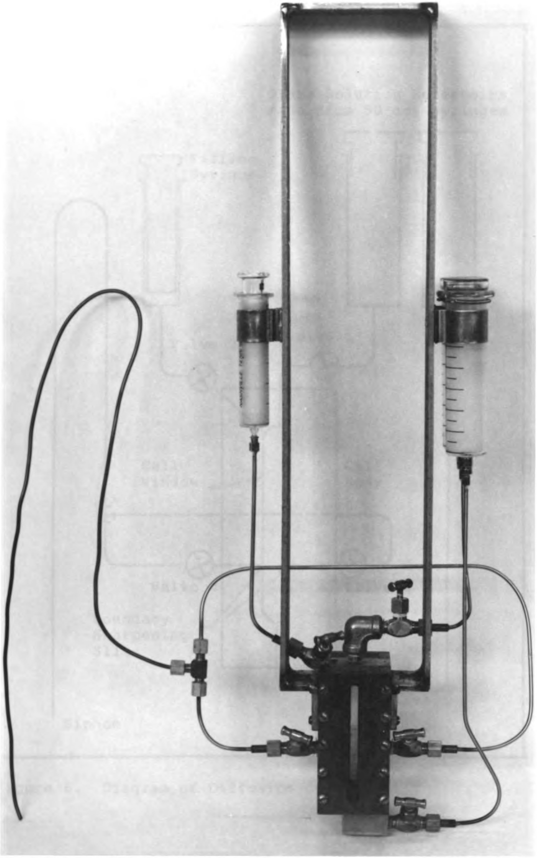


Figure 5. Photograph of Diffusion Cell for Measurement of Diffusion Coefficients.

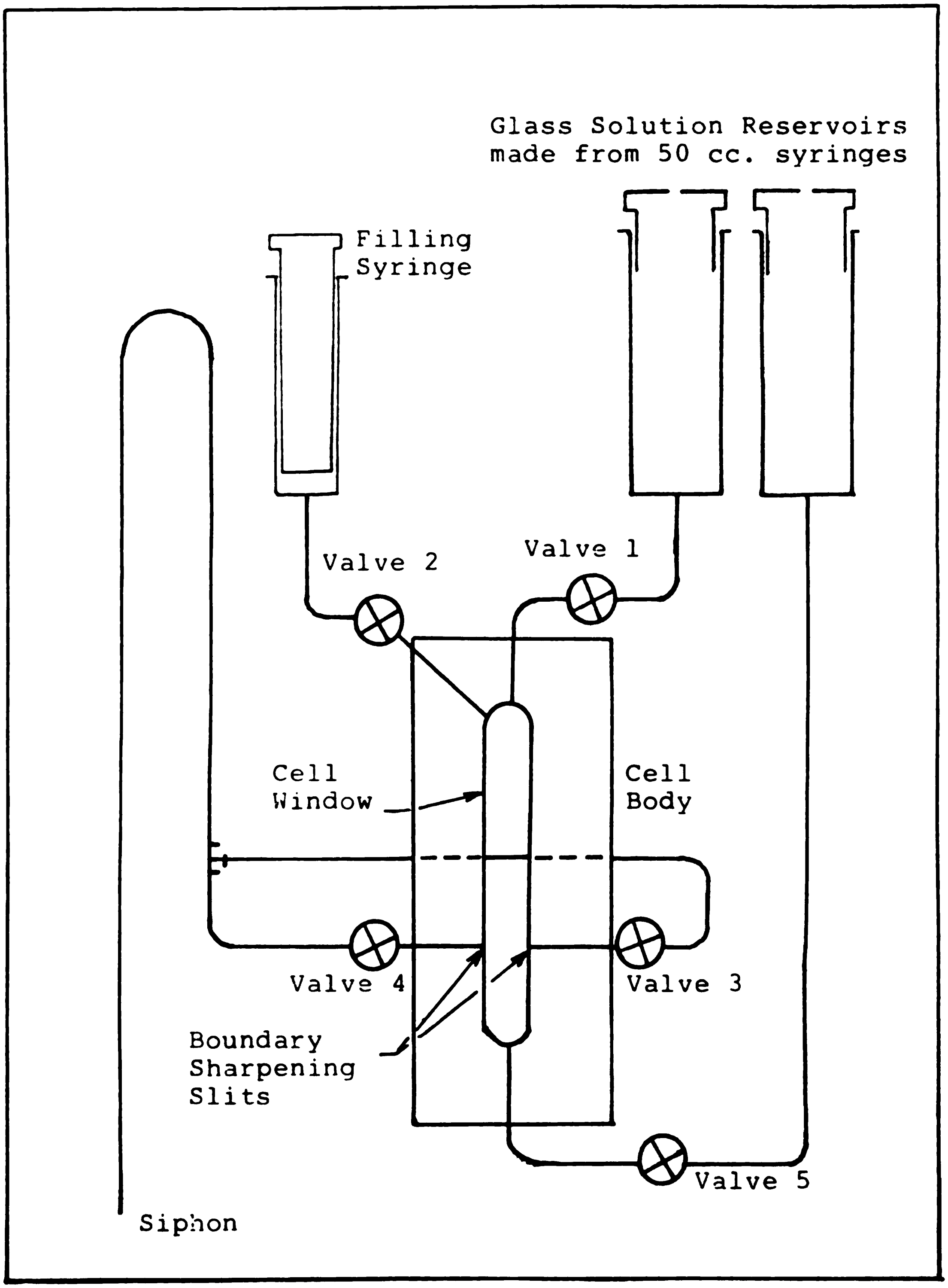


Figure 6. Diagram of Diffusion Cell.

cell, the denser solution through the bottom inlet and the lighter through the top, and out through the two outlets. A sharp boundary is thus formed between the two layered solutions. This boundary is located in the center of the lower beam. All the valves are then closed and the the solutions allowed to diffuse freely.

B. Experimental Procedure

The following procedure was found to be the most successful for measuring the binary diffusion coefficient in liquid polymer solutions:

(1) All cell valves except valve 2 are closed and, approximately 30cc of the less dense solution is placed in reservoir A. Some of this solution is then allowed to flow into the cell through valve 1 until the liquid level is about one inch above the outlets. Valve 1 is then closed.

(2) Valve 4 is then opened slightly and liquid is forced into the exit line by means of the syringe plunger until the liquid level in the cell is just above the outlets. Valve 4 is then closed and more solution from reservoir A is allowed to flow through valve 1 into the cell as in step (3). More liquid is forced into the exit line through valve 4, and the whole procedure repeated until liquid drips from the outlet line. This is done to ensure that liquid completely fills the exit line without air bubbles. This procedure is repeated using valve 3 until solution drips from the exit lines by siphon action.

(3) Valve 1 is opened next until the cell is completely filled with solution from reservoir A, then valve 2 is closed. Valve 5 is opened very slowly and solution allowed to flow into the line that connects

valve 5 to reservoir B. Valve 5 is closed when the line is filled with solution. Caution should be taken to prevent solution from entering reservoir B. At this point, all the exit and entrance lines including the cell are filled with the less dense solution.

(4) Reservoir B is then filled approximately to the same level as reservoir A with the more dense solution. During the filling, care should be taken to make sure that there are no air bubbles trapped between the syringe and the entrance line.

(5) The cell is then placed in position in the water bath. The reservoir valves (1 and 5) are opened one full turn followed slowly by valve 3, until the rate of flow from the exit line is one drop every 8 seconds. The opposite outlet valve (4) is then opened and adjusted until the combined exit flow rate is one drop every 4 seconds. It is very important to maintain balanced flow rates into upper and lower halves of the cell as well as through both outlets.

(6) Since the cell is originally full of less dense solution, it generally takes two to four hours for the more dense solution to rise to the level of the exit slits. The formation of a sharp interface is viewed through a telescope. Boundary formation is aided by the boundary sharpening slits in the two outlets. These slits allow the liquid to flow evenly out the entire width of the cell.

(7) When a satisfactory boundary is formed, valves 3 and 4 are closed followed by valves 1 and 5. The solutions are allowed to diffuse for some time (depending on the diffusion rate) until the fringes can be seen distinctly across the diffusion zone. Then the mirror which is used to reflect the image of the fringes into the telescope is swung away from the beam so that it is in view of the camera. The interference fringe patterns caused by the diffusion process are photographed at predetermined time intervals. A typical series of exposures taken for one run is shown in Figure 7.

(8) After the run is completed, the cell is drained and rinsed with solvent and acetone and dried with air.

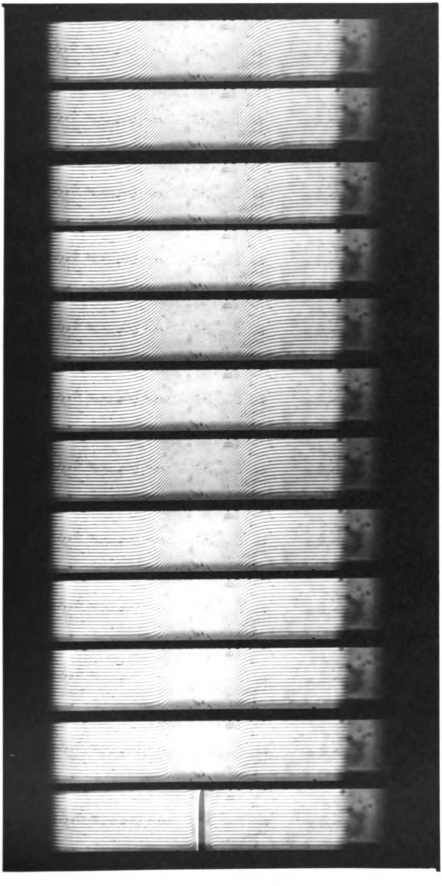


Figure 7. Typical Set of Photographs Taken During Diffusion Run.

C. Theory and Calculations

Consider a differential volume element in the diffusing section of the cell as shown in Figure 8. By setting up a material balance on the differential volume element which describes the mass transfer in and out of the element, we obtain

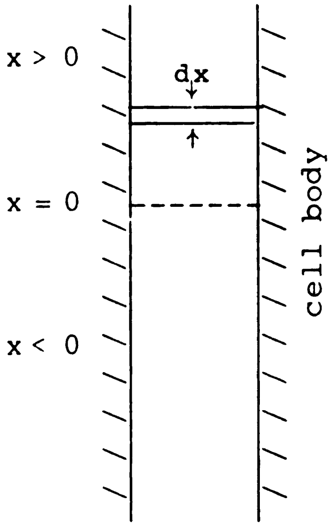


Fig. 8: Diffusion Cell Coordinates

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{D}\frac{\partial c}{\partial t} \qquad \text{(IV-1)}$$

with the following boundary conditions:

Case I $(x>0)$ i) $x \to \infty$ $t \geq 0$ $c = c_1$

ii) $t = 0$ $c = c_1$ $\infty > x > 0$

iii) $x = 0$ $c = (c_1 + c_1)/2$ $t \geq 0$

Case II $(x<0)$ i) $x \to -\infty$ $t \geq 0$ $c = c_2$

ii) $t = 0$ $c = c_2$ $0 > x > -\infty$

iii) $x = 0$ $c = (c_1 + c_2)/2$ $t \geq 0$

where c is the concentration and x is defined in Figure 8.

In order to solve equation (IV-1), it is necessary to make the following assumptions: (1) the concentration dependence of the diffusion coefficient D is negligible over the small concentration range involved, and (2) the diffusion gradient has the properties of normal distribution curves.

Equation (IV-1) may be solved with Laplace transforms or by other means to give the following identical solution for both case I and case II.

$$\frac{c - c_o}{c_2 - c_1} = \frac{1}{2} \text{ erf. } \left(\frac{x}{\sqrt{4Dt}}\right) \qquad \text{(IV-2)}$$

where c_o is the concentration at the zero position in the cell, and as a result of assumption (2) above, is equal to $\frac{1}{2}(c_1 + c_2)$. The refractive index, n, may be assumed proportional to the concentration, so that:

$$\frac{n - n_o}{n_2 - n_1} = \frac{1}{2} \text{ erf. } \left(\frac{x}{\sqrt{4Dt}}\right) \qquad \text{(IV-3)}$$

Essentially the fringe pattern is a plot of refractive index versus distance in the cell so that the refractive index difference may be represented by the number of fringes displaced. For the relationship between the method development and the fringe pattern, refer to Fig. 9, where J is the total number of fringes crossed from top to bottom; k is the local fringe number in the top half of the cell,

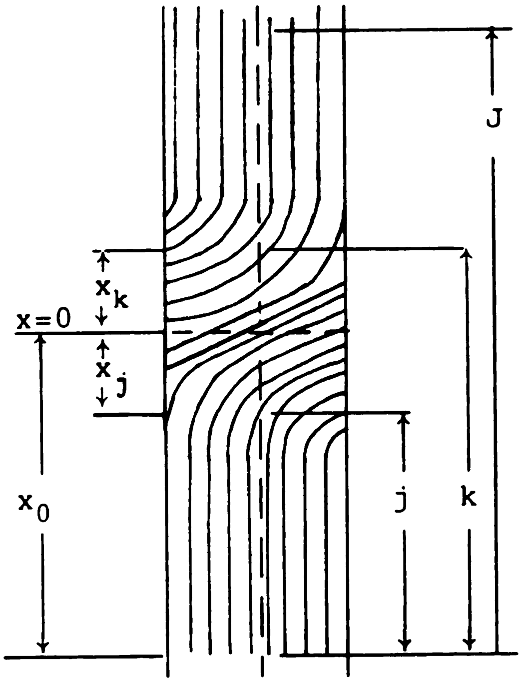


Figure 9. Fringe Pattern

and j is the local fringe number in the bottom half. Let x_j and x_k be the measured distance corresponding to fringes j and k respectively.

Thus, where $x > 0$

$$\frac{n - n_o}{n_2 - n_1} = \frac{k - \frac{1}{2}J}{J} = \frac{2k - J}{2J}$$

and equation (IV-3) becomes

$$\frac{x_k}{\sqrt{4Dt}} = \mathrm{erf}^{-1}\left(\frac{2k - J}{J}\right) \qquad \text{(IV-4)}$$

Similarly, where $x < 0$

$$\frac{n - n_o}{n_2 - n_1} = \frac{J - 2j}{2J}$$

and

$$\frac{x_j}{\sqrt{4Dt}} = \mathrm{erf}^{-1}\left(\frac{J - 2j}{J}\right) \qquad \text{(IV-5)}$$

The exact midpoint of the diffusion zone is difficult to determine; however, the distance, $X_k + x_j$, is easily determined by difference measurements. Therefore:

$$\frac{x_j}{\sqrt{4Dt}} + \frac{x_k}{\sqrt{4Dt}} = \mathrm{erf}^{-1}\left(\frac{J - 2j}{J}\right) + \mathrm{erf}^{-1}\left(\frac{2k - J}{J}\right) \qquad \text{(IV-6)}$$

The cell distance is not equal to the distance measured on the photographic plate because of the magnification of the image by a factor, M. Therefore:

$$\frac{x_j + x_k}{\sqrt{4Dt}} = \frac{x_j' + x_k'}{M\,\sqrt{4Dt}} \qquad \text{(IV-7)}$$

where x_j' and x_k' are distances on the photographic plate. Hence

$$Dt = \frac{1}{4M^2}\left[\frac{x_j' + x_k'}{\operatorname{erf}^{-1}\left(\frac{J - 2J}{J}\right) + \operatorname{erf}^{-1}\left(\frac{2k - J}{J}\right)}\right]^2 \qquad \text{(IV-8)}$$

For each exposure, value of the function

$$\left[\frac{x_j' + x_k'}{\operatorname{erf}^{-1}\left(\frac{J - 2j}{J}\right) + \operatorname{erf}^{-1}\left(\frac{2k - J}{J}\right)}\right]^2$$

were determined for several j's and k's and averaged. The averages for several exposures were plotted versus exposure time, and the slope of the resulting line was determined. Thus,

$$D = \frac{\text{slope}}{4M^2} \qquad \text{(IV-9)}$$

See Appendix A for details of a sample calculation.

This diffusion coefficient is assumed equal to the mutual diffusivity at the average concentration, $c_0 = \frac{1}{2}(c_1 + c_2)$.

The distances on the photographic plate were measured with an optical comparator made from a Gaertner microscope fitted with a traveling eyepiece. The traveling eyepiece could scan a total distance of 5 centimeters by turning a crank and the distance traveled was indicated on a vernier scale accurate to 0.0001 centimeters.

D. Calibration

For this study, the accuracy of the interferometric technique was established by measurement of the concentration-dependent diffusion coefficient for the binary system of sucrose-water at 25.0°C. This particular system was chosen because accurate, widely accepted diffusion data are available for comparison. The accuracy of the method used in this work was tested by comparing diffusion coefficients at 25.0°C for four aqueous sucrose solutions with those reported by Gosting and Morris [4D-1]. The data of Gosting and Morris have been carefully checked by several investigators [4D-2, 3, 4], and are thought to be accurate to ±0.2 percent. Gosting and Morris fit their data to the following empirical relationship using the least square technique:

$$D_s = 5.226\ (1 - 0.0148\ c_o) \times 10^{-6} \pm 0.002 \qquad \text{(IV-10)}$$

where D_S is the binary diffusion coefficient for sucrose-water system at 25.0°C, and c_o is the concentration of sucrose solution in grams of sucrose per 100 cm^3 of solution. A comparison of results are summarized in Table I. It is concluded that the precision of the interferometer is no worse than ± 2 percent.

Table I. Results of the Calibration Runs on the Interferometer.

Experimental Run No.	Concentration of Sucrose grams of sucrose/100 C.C.	Diffusion Coefficient ($\times 10^6 cm^2/sec$)		Percentage Deviation
		Ref. [5D-1]	This Work	
1	0.8	5.164	5.213	+ 0.948
2	1.0	5.148	5.224	+ 1.476
3	1.4	5.118	5.098	- 0.391
4	0.4	5.178	5.150	- 0.541
			Standard Deviation	0.888

E. Error Analysis

Some sources of error in measurement of diffusion coefficients include:

(1) The accuracy in determining the fraction of a fringe when measuring the total fringes for a particular exposure. The percentage error increases as the total number of fringes decreases.

(2) The assumption that the concentration dependence of diffusion coefficient is negligible over the narrow concentration range involved in the experimental run.

(3) The accuracy of the magnification factor of the camera.

(4) Error in measuring distances between fringes on the photographic plate.

(5) The accuracy in determining the slope defined by equation (IV-9).

The average percentage error of diffusion coefficients obtained in this work is estimated to be within ± 2 percent.

V. THERMODYNAMICS OF ASSOCIATING POLYMER SOLUTIONS

A. Methods for Detecting Association of Polymer Molecules in Solution [5A-1]

The purpose of this section is to review the methods available for a quantitative evaluation of solutions containing associating polymer molecules. A quantitative description is needed for correct interpretation of associating solution properties.

The phenomenon of association is discussed in the literature under different names: aggregation, self-association, multimerization, complex formation, etc. All processes leading to the formation of complexes of higher particle weight from molecules of lower molecular weight via physical bonds can be called sociation processes. They may occur between like molecules or unlike molecules. The sociation process between like molecules is called "multimerization." Solvation is restricted to the sociation process between solute and solvent. A non-multimerized molecule is called a unimer. Like unimers of molecular weight $\overline{M}_I$ can multimerize to form a particle of weight $\overline{M}_n$. The multimerization number n describes the number of unimers in a multimer particle. Homologue series of polymer molecules with like constitution are considered as like molecules.

Basically, two groups of methods can be used to detect and determine multimers: group specific methods and molecule specific methods. Group specific methods look at the structure of a group and its interaction with other groups. Typical examples of group specific methods are spectroscopic methods (such as infrared or ultraviolet) and nuclear magnetic resonance. Molecule specific methods look at the molecule as a whole, e.g., their molecular weight and/or their volume. Typical examples are membrane and vapor pressure osmometry, light scattering, ultracentrifugation, viscometry and gel permeation chromatography.

A multimerizing polymer molecule may have only few associogenic groups. Because these are only a small fraction of the total groups present, they may escape detection by group specific methods which typically become insensitive at levels of about 1% "impurities." The particle weight of the multimers may, however, increase drastically. One associogenic group in a polymer with a degree of polymerization of one thousand represents only 0.1% of the total groups, but the particle weight increases 100% if dimerization is complete.

Obviously, molecule specific methods are the prime choice for the detection and determination of multimerizations. It should be remembered, however, that they are influenced by intermolecular interactions only. Information on intramolecular association and the structure of multimers is difficult to get from molecule specific methods. Therefore, both molecule and group specific methods must be employed in order to elucidate the multimerization process.

B. Types of Association in Polymer Solutions

Two basic types of association may be distinguished: open and closed association. Open association [5B-1, 2] is a consecutive association in which all types of multimers appear:

$$\begin{aligned}
&A_1 + A_1 \xrightleftharpoons{K_2} A_2 \\
&A_1 + A_2 \xrightleftharpoons{K_3} A_3 \\
&A_1 + A_3 \xrightleftharpoons{K_4} A_4 \qquad \text{(V-1)} \\
&- - - - - - - - \\
&A_1 + A_{n-1} \xrightleftharpoons{K_n} A_n
\end{aligned}$$

where A_i represents i-mer and K_i is the association equilibrium constant of the formation of i-mer. Closed association exhibits an all-or-none process in which only unimers and n-mers are present:

$$n\,A_1 \xrightleftharpoons{K_c} A_n \qquad \text{(V-2)}$$

where K_c is the equilibrium constant of the n-merization process.

Combinations of these types of equilibria are of course possible. However, discussions throughout this paper will be restricted to open association because open association seems to be the most important type for synthetic polymer molecules in solutions. Moreover, it has been shown [5B-2] that a curve fitting using closed association models can very often be replaced by using an open association model with only one equilibrium constant.

Association may be further subdivided according to the variation of the number of associogenic sites per molecule with the degree of polymerization in polymer homologeous series. The number of groups capable of association may be constant for each molecule, regardless of its length. A simple example is a linear unipolymer chain with associating endgroups. This type of association can thus be called "end-to-end" association. This term should not imply that this type of association occurs exclusively via endgroups. It should merely indicate that the number of associogenic groups per polymer molecule is independent of its length.

On the other hand, the number of associogenic groups may increase proportionally to the chain length. Associogenic groups may be special groups or sequences of constitutional or configurational groups. This type of association can thus be called "segment-to-segment" association.

In the case of end-to-end association, the proper choice for describing the polymer concentration should be molar concentratiion, whereas in segment-to-segment association the association equilibrium constants have to be based on the mass concentrations. This work deals exclusively with open end-to-end association. For those who are interested in segment-to-segment and/or closed associations, references can be found elsewhere [5B-2, 3, 4].

C. Thermodynamics of Solutions Containing Associating Polymer Species

The present section is concerned with strong orientational effects of polymers on the thermodynamics of polymer solutions. Important and typical examples are solutions containing associating polymer molecules with specific functional endgroups. The foundation of most existing polymer solution theories (such as those discussed in Chapter II) are based primarily on the assumption that the polymer molecules are homogeneously distributed throughout the solution. This assumption is expected to break down when strong intermolecular interaction (e.g., hydrogen bonding) occurs between polymer molecules. Since the interaction energy of hydrogen bonding is very large compared to other intermolecular energies, methods like the perturbation approach applied in statistical thermodynamics to account for effects of weak intermolecular interactions often become useless. In fact, there exists at present no satisfactory theory of strong orientational effects from which one may deduce the thermodynamic properties and especially the excess functions from intermolecular forces and properties of the pure components.

In the history of thermodynamics of solutions, the earliest and probably the most popular approach for describing solution properties of associating solutions is the "chemical approach" first proposed by Dolezalek [5C-1]. Although Dolezalek's association model gained some success in interpreting the negative deviations from Raoult's law in some systems, his oversimplified picture of associating solutions also drew serious criticism. However, it remains as a good basis for the treatment of associating solutions in which specific interactions do exist between molecules.

The remaining part of this section is dedicated to presenting an association model developed by the author for dilute solutions of associating polymers in inert solvents. This association model describes favorably the thermodynamic properties of associating polymer solutions, and provides good explanations for some discrepancies that exist between experimental data in the literature and theoretical predictions of existing polymer solution theories.

Consider a polymer-solvent mixture in which polymer molecules associate with each other to form larger particles according to the open associating process described by equation (V-1). The solvent molecules of the system are assumed to form no associates with either solvent or polymer molecules. It is also assumed that there is no overall volume change of solution due to intermolecular association and the association constant is independent of molecular size,

$$K_2 = K_3 = \text{- - -} = K_n = K \qquad \text{(V-3)}$$

All i-mer concentrations can be related by the association constant, K.

$$C_2 = K\ C_1^2$$

$$C_3 = K^2\ C_1^3$$

\- - - - - - -

$$C_i = K^{i-1}\ C_1^i \qquad \text{(V-4)}$$

\- - - - - - -

$$C_n = K^{n-1}\ C_1^n$$

where C_i is the molar concentration of i-mer. Since the true molar concentration of polymer solute, C_P, is the sum of the molar concentrations of all i-mers,

$$C_P = \sum_{i=1}^{n} C_i$$

$$= C_1 + K\ C_1^2 + K^2\ C_1^3 + --- + K^{n-1}\ C_1^n \qquad \text{(V-5)}$$

Also since the molar concentration of (i+1)-mer is always less than that of i-mer (otherwise C_P will not be finite),

$$K\ C_1 = C_2/C_1 < 1 \qquad \text{(V-6)}$$

therefore, the true molar concentration of polymer solute can be expressed as:

$$C_P = \frac{C_1}{1 - K\ C_1} \qquad \text{(V-7)}$$

which can be rewritten:

$$C_1 = \frac{C_P}{1 + K\ C_P} \qquad (V\text{-}8)$$

It can be seen from equation (V-5) that C_P represents the concentration of "kinetically independent" polymer molecules per unit volume of solution.

The osmotic pressure of a polymer solution can be expressed in terms of a virial expansion according to statistic thermodynamics [5C-2].

$$\frac{\Pi}{\rho_P\ R\ T} = \frac{1}{\overline{M}_N} + A_2\ \rho_P + A_3\ \rho_P^2 + --- \qquad (V\text{-}9)$$

where A_2, A_3, etc., are the osmotic virial coefficients, Π is the osmotic pressure of the polymer solution at concentration ρ_P (in grams of polymer per unit volume of solution), and $\overline{M}_N$ is the number average molecular weight of polymer solute. For most non-associating polymer-solvent systems, plots of Π/ρ_P versus ρ_P are found to be linear in the dilute concentration range as predicted by equation (V-9). The slope of the plot is equivalent to the second virial coefficient, and extrapolation of the plot to zero concentration gives the reciprocal of the number average molecular weight of the polymer. Equation (V-9) also predicts that for a non-associating theta solution (a theta solution is defined as a solution in which all virial terms in equation (V-9) vanish), $\Pi/\rho_P\ R\ T$ is independent of concentration and is equivalent to the reciprocal "true" number average molecular weight,

$$\left(\frac{\Pi}{\rho_P \; R \; T}\right)_\theta = \frac{1}{\bar{M}_N} \qquad \text{(V-10)}$$

However, for associating polymer-solvent systems, the true number average molecular weight in equation (V-10) should be replaced by ρ_P/C_P,

$$\left(\frac{\Pi}{\rho_P \; R \; T}\right)_\theta = \frac{1}{\rho_P/C_P} \equiv \frac{1}{(\bar{M}_N)_{app,\theta}} \qquad \text{(V-11)}$$

Equation (V-11) also serves as the definition of the apparent number average molecular weight at theta condition. It should be noted that $(\bar{M}_N)_{app,\theta}$ is an increasing function of concentration with its functionality depending on the type of association [5C-3].

In analogy to non-associating systems, we may write [5C-4]:

$$\frac{\Pi}{\rho_P \; R \; T} = \frac{1}{(\bar{M}_N)_{app,\theta}} + A_2^* \rho_P + A_3^* \rho_P^2 + \ldots \qquad \text{(V-12)}$$

for associating systems not at theta condition. By doing so, we actually assume that all intermolecular associating forces between polymer molecules can be separated from all other interactions of the components. The superscript star is added to individual virial coefficients because they are different from the corresponding virial coefficients defined in equation (V-9) in that those in equation (V-12) are for the associated complexes (multimers).

Since the mass concentration of solute is given by:

$$\rho_P = \sum_{i=1}^{n} C_i \overline{M}_i = \overline{M}_N \sum_{i=1}^{n} iC_i \qquad (V-13)$$

where $\overline{M}_i$ represents the average molecular weight of i-mer. Substitution of equation (V-8) and (V-13) into equation (V-11) yields:

$$(\overline{M}_N)_{app,\theta} = \overline{M}_N + \frac{K\rho_P \overline{M}_N}{(\overline{M}_N)_{app,\theta}} \qquad (V-14)$$

Equation (V-14) is the concentration dependence of apparent number average molecular weight for theta solutions with consecutive associations. The result has been previously derived by Meyer and van der Wyk [5C-5], and also by Solc and Elias, using a more rigorous approach [5C-4]. It is convenient to define α, the "degree of association" as:

$$\alpha = \frac{\sum_{i=1}^{n} i\ C_i}{\sum_{i=1}^{n} C_i} = \frac{(\overline{M}_N)_{app,\theta}}{\overline{M}_N} \qquad (V-15)$$

Combining equations (V-14) and(V-15) gives:

$$\alpha = 0.5\ [1 + (1 + \frac{4K\rho_P}{\overline{M}_N})^{\frac{1}{2}}] \qquad (V-16)$$

When there is no association (K=0) α equals 1.0. It can be seen from equation (V-16) that the degree of association is an increasing function of polymer concentration. Equation (V-14) can be rearranged to:

$$(\overline{M}_N)^{-1}_{app,\,\theta} = \overline{M}_N^{-1} - \frac{K\rho_P/(\overline{M}_N)_{app,\theta}}{\overline{M}_N\left(1+\frac{K\rho_P}{(\overline{M}_N)_{app,\theta}}\right)} \qquad \text{(V-17)}$$

Realizing that $\alpha = (\overline{M}_N)_{app,\,\theta}/\overline{M}_N$, equation (V-17) can be reduced to a more compact form:

$$(\overline{M}_N)^{-1}_{app,\,\theta} = \overline{M}_N^{-1} - \frac{\frac{K\rho_P}{\alpha\overline{M}_N}}{\overline{M}_N\ \left(1 + \frac{K\rho_P}{\alpha\overline{M}_N}\right)} \qquad \text{(V-18)}$$

Equation (V-18) is a more convenient form of equation (V-14), since $(\overline{M}_N)^{-1}_{app,\,\theta}$ is an explicit function of concentration in equation (V-18). It describes the variation of the number of kinetically independent molecules as a function of concentration in the absence of all other interactions. Substituting equation (V-18) into equation (V-12), one gets:

$$\frac{\Pi}{\rho_P\ R\ T} = \left(\frac{1}{\overline{M}_N} + A_2^\star\ \rho_P + A_3^\star\ \rho_P^2 + \ldots\right) - \frac{\frac{K\rho_P}{\alpha\overline{M}_N}}{\overline{M}_N\ \left(1 + \frac{K\rho_P}{\alpha\overline{M}_N}\right)} \qquad \text{(V-19)}$$

or

$$\frac{\Pi}{R\,T} = \left(\frac{1}{\underline{V}} + \frac{A_2^* \, \overline{M}_N^2}{\underline{V}^2} + \frac{A_3^* \, \overline{M}_N^3}{\underline{V}^3} + \ldots\right) - \frac{K/\alpha}{\underline{V}\,(\underline{V} + K/\alpha)} \qquad \text{(V-20)}$$

where

$$\underline{V} \equiv \overline{M}_N/\rho_P \qquad \text{(V-21)}$$

$\underline{V}$ represents the average volume occupied by one mole of nonassociated polymer molecules (unimers).

According to excluded volume theory, the third virial coefficient A_3 is closely related to the second virial coefficient A_2 by the relation:

$$A_3 \doteq g\, A_2^2\, \overline{M}_N \qquad \text{(V-22)}$$

where g is a constant for a particular polymer-solvent system and is a measure of "goodness" of the solvent. The value of g should range from zero for a theta solvent to an asymtotic limit of 4/3 for a good solvent [5C-6]. If we assume that the relation between A_2 and A_3 (equation (V-22)) is also valid for A_2^* and A_3^* and g = 1, equation (V-20) can be approximated to:

$$\frac{\Pi}{RT} = \frac{1}{\underline{V} - B} - \frac{K/\alpha}{\underline{V}\,(\underline{V} + K/\alpha)} \qquad \text{(V-23)}$$

where $B = A_2^* \, \overline{M}_N^2$ (V-24)

In a very dilute solution or when the association is relatively weak,

$$K/\alpha << \underline{V} \tag{V-25}$$

and equation (V-23) can be reduced further to:

$$\frac{\Pi}{R\ T} = \frac{1}{\underline{V} - B} - \frac{K/\alpha}{\underline{V}^2} \tag{V-26}$$

The assumption of g = 1 made to arrive at equations (V-23) and (V-26) introduces minor error in evaluating the osmotic pressure of moderately concentrated solutions. However, the error should be negligible for dilute polymer solutions in which we are most interested.

Zimm [5C-7] pointed out the exact formal correspondence between the osmotic pressure equation (i.e., equation (V-9)) and the virial equation of state of an imperfect gas. It is interesting to note that a similar formal correspondence also exists between equation (V-26) and the well-known van der Waals equation of gas,

$$\frac{P}{RT} = \frac{1}{v - b} - \frac{a}{v^2} \tag{V-27}$$

where v is the molar volume of the gas under pressure P and temperature T. The parameter b accounts for the finite volume of the gas molecules with its value depending on the size and nature of the gas molecules and the term a/v^2 is a correction made to account for the attractive forces that exist between molecules. The analogy between the two equations is hardly surprising considering the similarities that exist between the two systems. The osmotic pressure equation derived according to the associating polymer solution model is analogous to the van der Waals equation, not only in form but also in the physical meaning of the corresponding parameters. In equation (V-26), the term $(K/\alpha)\underline{V}^2$ accounts for effects of intermolecular attraction of polymer molecules via specific (such as hydrogen bonding) and/or non-specific (such as van der Waals) interacting forces. The meaning of parameter B in the association model is not very clear from its definition (i.e. equation (V-24)). To understand the physical significance of B, we have to first understand the physical meaning of A_2 the second virial coefficient. In fact, Zimm [5C-7] has shown that A_2 can be directly related to $\underline{u}$, the volume excluded to a particular polymer molecule due to the presence of other polymer molecules in solution, by the relation

$$A_2 = \frac{N_A \underline{u}}{2\overline{M}_N^2} \tag{V-28}$$

where N_A is the Avagadro constant and $\overline{M}_N$ the number average molecular weight of polymer molecules. The parameter B, therefore, represents molar excluded-volume of polymer molecules in solution since

$$B = A_2\overline{M}_N^2 = N_A\underline{u}/2 = \text{Molar excluded volume} \tag{V-29}$$

The difference between $\underline{V}$ and B can therefore be considered as "molar free volume" of polymer molecules in solution.

Taking a linear expansion of equation (V-14) for

for $(\overline{M}_N)^{-1}_{app,\ \theta}$ followed by substitution into equation (V-12) yields:

$$\frac{\Pi}{\rho_P RT} = \frac{1}{\overline{M}_N} + (A_2^{\star} - \frac{K}{\overline{M}_N^2})\ \rho_P + (A_3^{\star} + \frac{2K^2}{\overline{M}_N^3})\ \rho_P^2 + \ldots \tag{V-30}$$

$$= \frac{1}{\overline{M}_N} + (A_2)_{obs}\ \rho_P + (A_3)_{obs}\ \rho_P^2 + \ldots$$

where

$$(A_2)_{obs} = A_2^{\star} - \frac{K}{\overline{M}_N^2} \tag{V-31}$$

$$(A_3)_{obs} = A_3^{\star} + \frac{2K^2}{\overline{M}_N^3} \tag{V-32}$$

As can be seen from equations (V-31) and (V-32), the observed virial coefficients of an associating polymer-solvent system have two contributions: a term identified with association, and a second term which might be identified with all other interactions.

D. Presentation of Osmometry Data and Discussions

The osmotic pressure of PTHF-MEK solutions were measured using a Hallikainen automatic membrane osometer (Model 1361 - Code D) designed by Shell Development Co. The details of the osmometer and the experimental procedures were discussed in Chapter III. Sartorius regenerated cellulose (Code SM-11539) with pore size <5 mm was employed throughout this work. Four monodisperse polytetrahydrofurane (PTHF) samples, designated as A1, A2, B1, and B2, were purchased from Polymer Laboratories, Ltd. (Church Stretton, Shrewsbury, U.K.), and their characteristics are listed in Table II. The polymer samples were used without further purification.

Table II. Characteristics of PTHF Samples.

Polymer Code	$\overline{Mn}$	Polydispersity	End-Groups
A1	281,000	<1.05	$-CH_3$
A2	30,000	<1.05	$-CH_3$
B1	7,660	<1.05	-OH
B2	2,500	<1.05	-OH

The results are listed in Tables III and IV and also plotted as Figure 10. As can be seen from Figure 10, the agreement between experimental data and theoretical predictions of the association model is good. The significant difference in the characteristics of the two plots in

Table III. Concentration Dependence of Reciprocal Apparent Number Average Molecular Weights of PTHF-A2-MEK Solutions at 34.0°C

Polymer	Concentration (grams/dl)	$\Pi/\rho_p RT \times 10^{+4}$ (moles/grams)	
		Calculated*	Experimental
PTHF-A2	0.0521	0.3551	0.3570
	0.1190	0.3857	0.3916
	0.1640	0.4055	0.3988
	0.2553	0.4450	0.4414
	0.3036	0.4657	0.4680
	0.3538	0.4876	0.4839
Root Mean Square Deviation:		0.0047	

$\overline{M}_N$ = 29,900 grams/mole

A_2 = 0.0043 mole cc/gram^2

*Calculation based on equation (VI-9) using least square technique to fit the data.

Table IV. Concentration Dependence of Reciprocal Apparent Number Average Molecular Weights of PTHF-B1-MEK at 34.0°C.

Polymer	Concentration (Grams/dl)	$\Pi/\rho_p RT \times 10^{+4}$ (moles/gram)		
		Calculated*	Calculated†	Experimental
PTHF-B1	0.0235	1.0719	1.0643	1.0677
	0.0336	1.0208	1.0271	1.0259
	0.0449	0.9797	0.9900	0.9898
	0.0749	0.9196	0.9168	0.9082
	0.0802	0.9140	0.9076	0.9197
	0.1074	0.8999	0.8781	0.8754
	0.1226	0.9008	0.8749	0.8729
	0.1990	0.9695	0.9962	0.9966
Root Mean Square Deviation		0.0184	0.0059	

*Calculated using association model (equation (V-26)) ($\bar{M}_N$= 7,660 grams/mole, $A_2^* = 0.015$ mole cc/gram^2, $K = 1.07 \times 10^7$ cc/mole)

†Calculated using non-association model (equations (V-9) and (V-22) ($\bar{M}_N$= 8,570 grams/mole, $A_2^* = -0.0483$ mole cc/gram^2, g = 0.997).

Figure 10. Concentration Dependence of Reciprocal Apparent Number Average Molecular Weight of PTHF-MEK Solutions at 34.0° C.

○ PTHF-B1-MEK
△ PTHF-A2-MEK

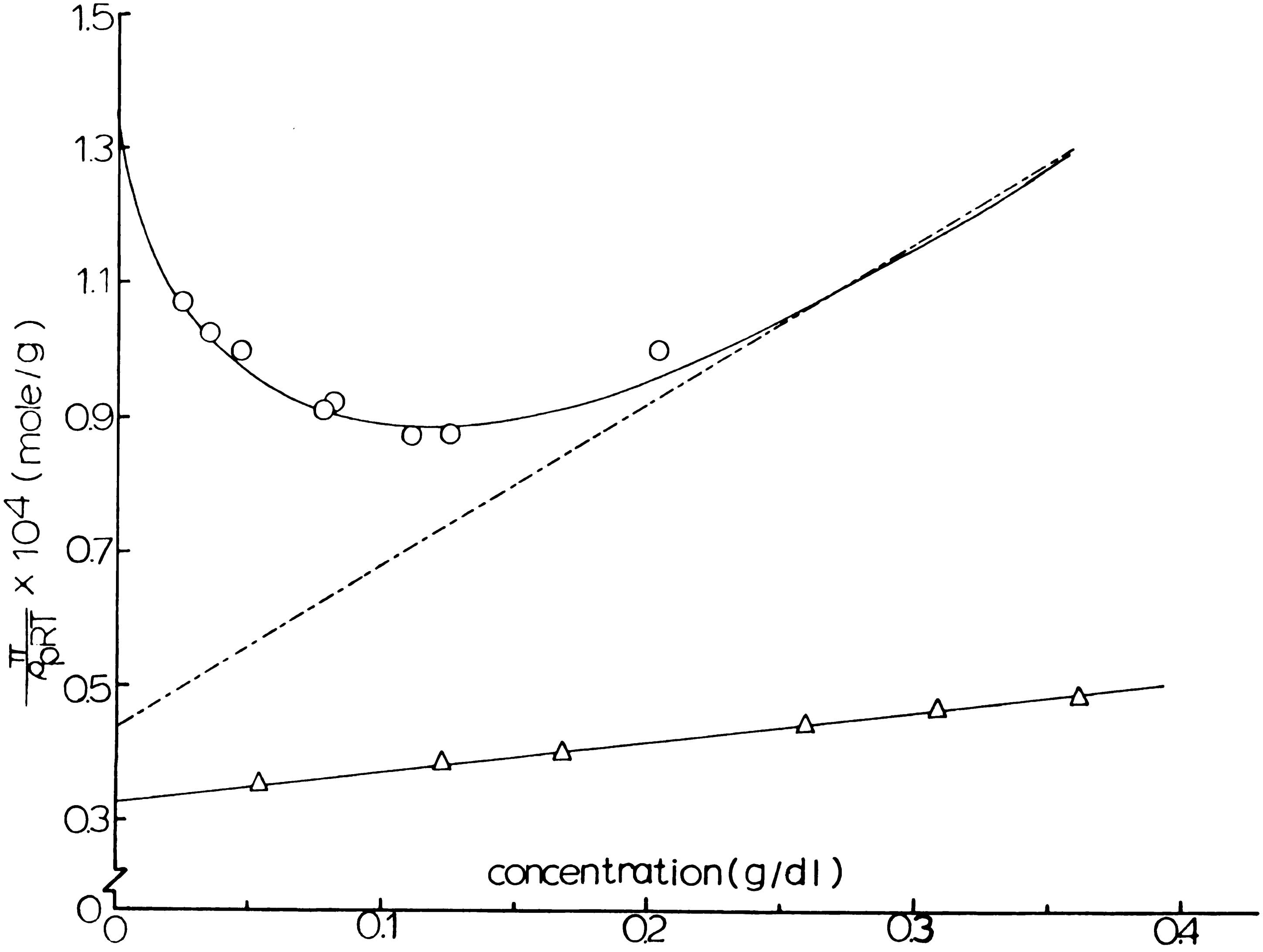

1.5
1.3
1.1
0.9
0.7
0.5
0.3
0
$\frac{\pi}{\rho RT} \times 10^4$ (mole/g)
0
0.1
0.2
0.3
0.4
concentration(g/dl)

Figure 10. Concentration Dependence of Reciprocal Apparent Number Average Molecular Weight of PTHF-MEK Solutions at 34.0° C.

○ PTHF-B1-MEK
△ PTHF-A2-MEK

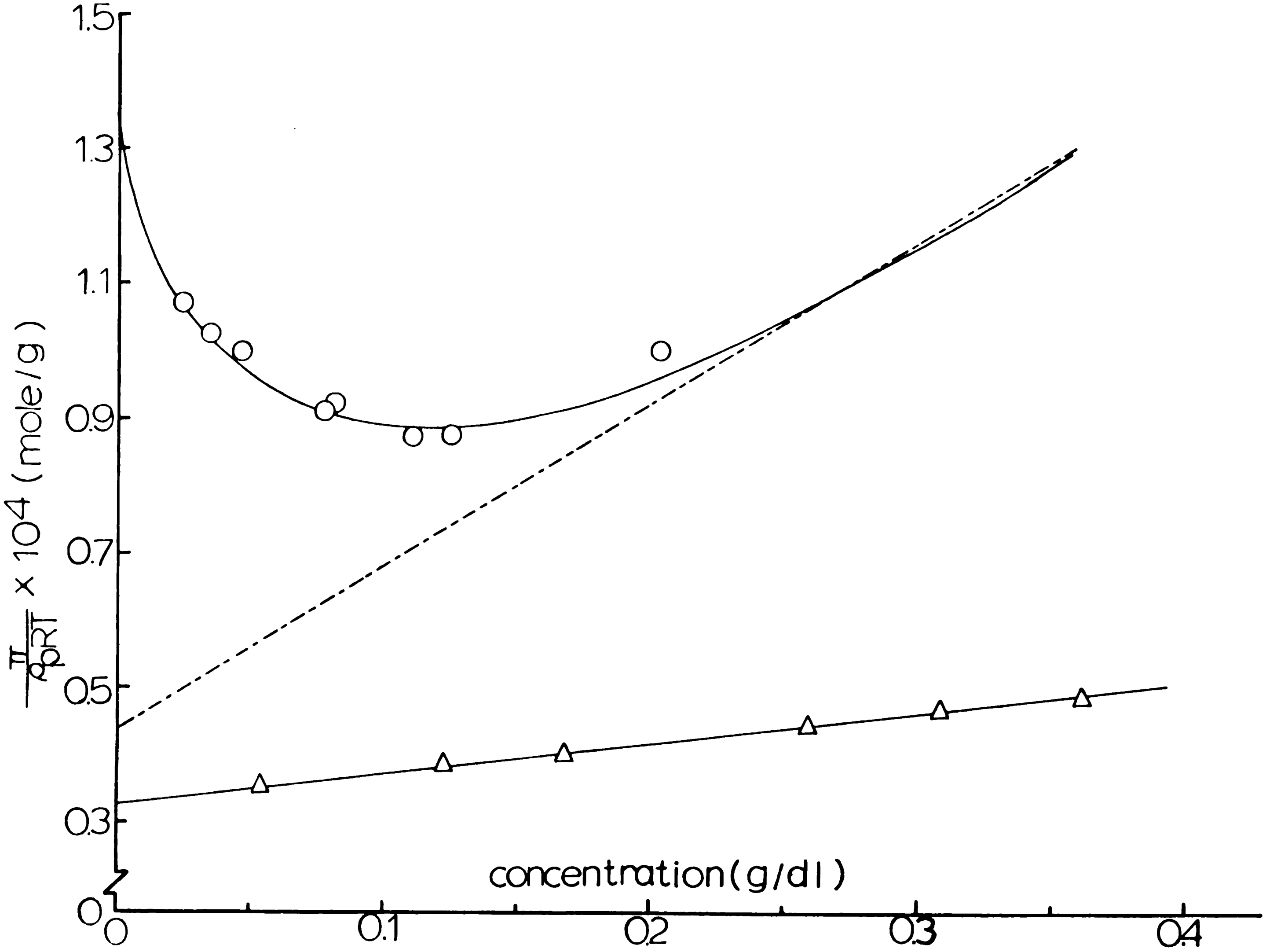

1.5
1.3
1.1
0.9
0.7
0.5
0.3
0
$\frac{\pi}{\rho RT} \times 10^4$ (mole/g)
concentration(g/dl)
0
0.1
0.2
0.3
0.4

Figure 10 seems to indicate that PTHF-B1 molecules associate to form complexes via OH end-groups in MEK. No evidence indicates any detectable association between PTHF-A2 molecules.

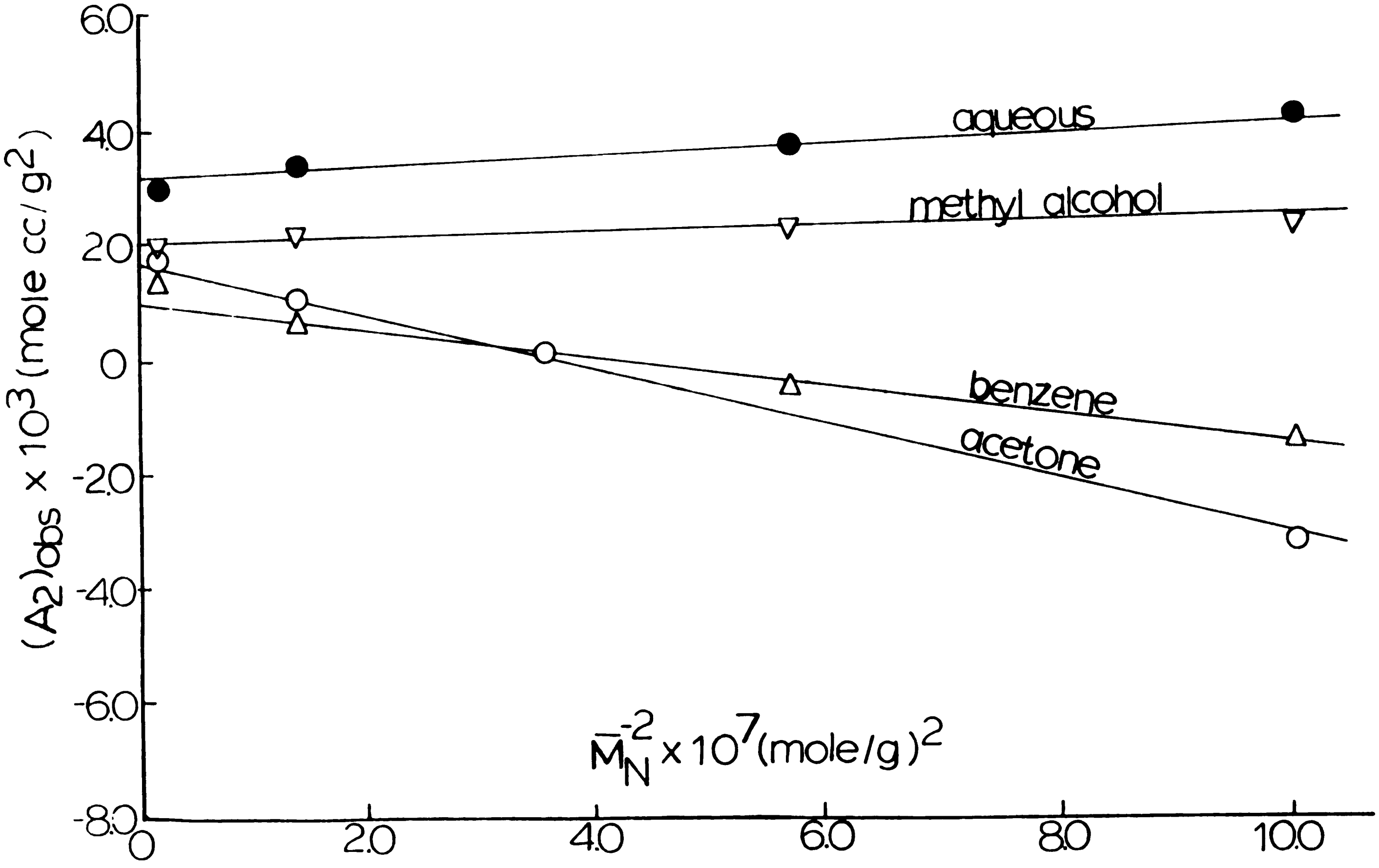
The second virial coefficient A_2 of the PTHF-B1-MEK solution is found, based on the non-association model, to be negative and much smaller than A_2 of PTHF-A2-MEK solution. This finding conflicts with excluded volume theory [5D-1], which predicts that A_2 should decrease very slowly with increasing polymer molecular weight. Similar findings have also been reported by other investigators for polyvinyl chloride-cyclohexanone solution [5D-2] and for polyethylene oxide-benzene and -acetone solutions [5D-3, 4, 5]. Although the excluded volume theory allows A_2 to have a small negative value when weak intermolecular attraction exists in the system, large negative A_2 and change of sign of A_2 from positive for higher molecular weight to negative for lower molecular weight polymer are not predicted and cannot be explained by the theory. It is concluded, therefore, that the excluded volume theory should be restricted to non-associating polymer-solvent systems only. Moreover, A_2 is traditionally regarded as a measure of "goodness" of solvents for polymer solutes, and a large negative value of A_2 for PTHF-MEK solution at 34.0°C would mean MEK is a non-solvent to PTHF. This conflicts the observation that MEK is a theta solvent to PTHF at 25.0°C (that means MEK should be a better-than-theta solvent to PTHF at the higher temperature). In fact, PTHF dissolves readily in MEK to form a homogeneous solution at 34.0°C. The author suggests that it is A_2^*, instead of $(A_2)_{obs}$, which should be used as a measure of solvation power of solvents for associating polymer-solvent systems in which polymer molecules associate with each other mainly via their end-groups.

The conflicts existing between experimental results and theoretical predictions discussed in the preceeding paragraph can be explained by the association model presented in section C of this chapter. If we accept the prediction by excluded volume theory that the second virial coefficient is insensitive to polymer molecular weight and the assumption made earlier that the association constant K is independent of polymer molecular weight, equation (V-31) predicts that a plot of $(A_2)_{obs}$ vs. $\overline{M}_N^{-2}$should be linear with intercept equivalent to A_2^* and slope -K. Equation (V-31) suggests that the observed second virial coefficient $(A_2)_{obs}$ decreases with decreasing polymer molecular weight when the association term $K/\overline{M}_N^2$ is significant comparing to the virial term A_2^*. According to the equation, the observed second virial coefficient is also expected to change its sign from positive to negative as the polymer molecular weight continues to decrease such that the association term becomes greater than the virial term A_2^*. In order to verify the validity of these predictions the data of Yamada and co-workers [5D-3] for the second virial coefficient of polyethyleneglycol (PEG) solutions were replotted in a manner as suggested by equation (V-31). Figure 11 shows that the agreement between the straight-line prediction and experimental results is surprisingly good. In aqueous or methyl alcohol solution, the OH end-groups of PEG are surrounded by solvent molecules, and are most likely to form hydrogen bonds with them. Intermolecular association of PEG molecules via OH end-groups is therefore expected to be very weak. Among the four solvents under study, the association constant of PEG is found to be greatest in acetone. Figure 11 also suggests that water is a better solvent for PEG than the others because PEG has the highest A_2^* value in water.

The larger and positive A_2^* of the PTHF-B1-MEK solution, when compared to the value of A_2 for PTHF-A2-MEK solution, is consistent with excluded volume theory, although the difference between the two values is greater than what would be expected. A possible explanation for the discrepancy is that some of the normally non-associating intermolecular attraction forces actually contribute to the association mechanism when hydrogen bonding occurs. Thus, some of the non-associating effects in A_2 are actually shifted to the association term.

According to excluded volume theory, the value of g defined by equation (V-22) should vary from zero for a theta solvent to a asymtotic limit of 4/3 for a good

Figure 11. Molecular Weight Dependence of Observed Second Virial Coefficient of PEG Solutions (Replotted from reference [5D-3].


6.0
4.0
2.0
0
-2.0
-4.0
-6.0
-8.0
$(A_2)_{obs} \times 10^3$ (mole cc/g^2)
aqueous
methyl alcohol
benzene
acetone
$\bar{M}_N^{-2} \times 10^7$(mole/g)^2
0
2.0
4.0
6.0
8.0
10.0

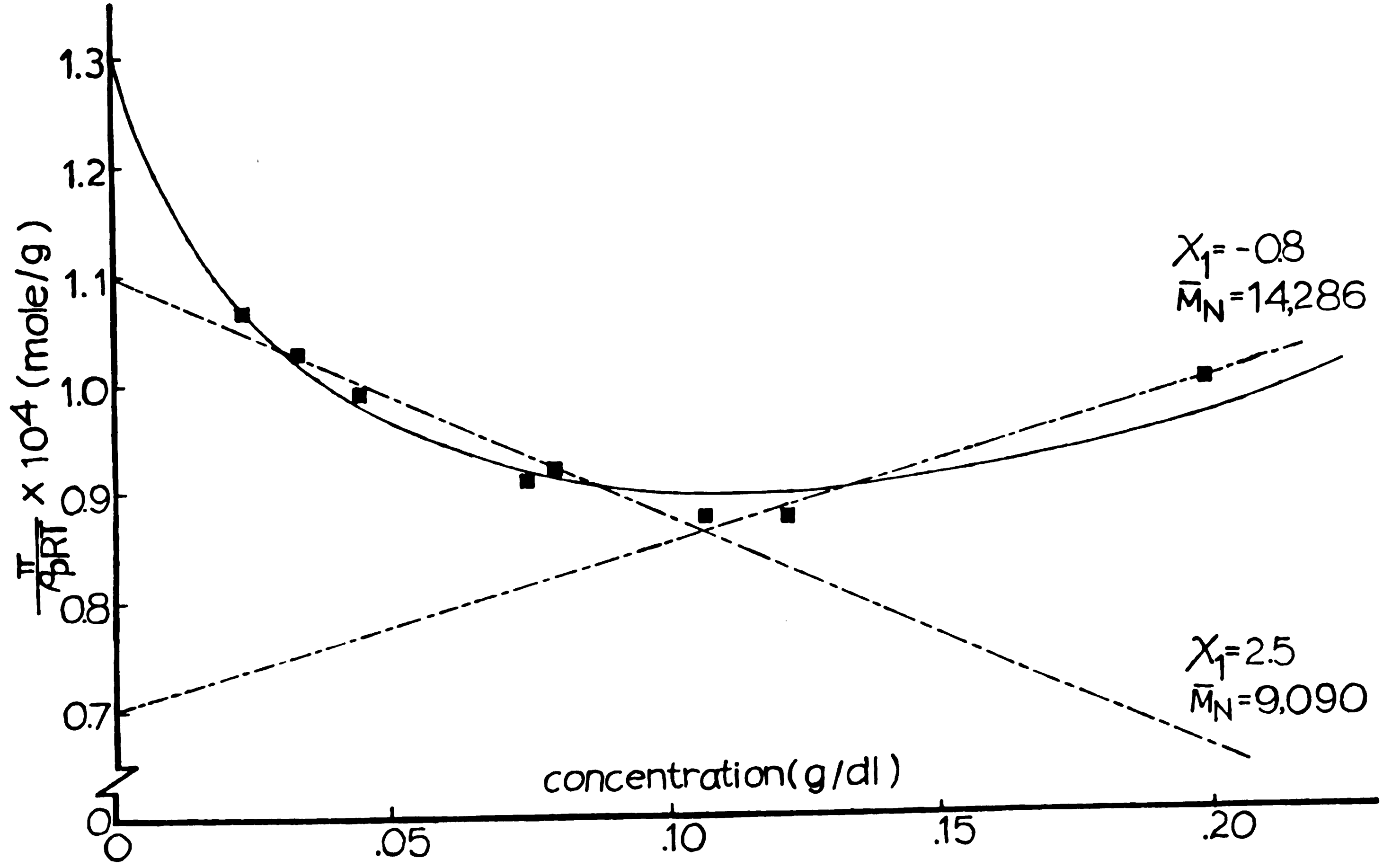
solvent. This prediction is again not confirmed by the data of Nord and co-workers for polyvinyl alcohol-acetate copolymer in aqueous solution [5D-6]. Inspection of their data indicates that the g values of their eighteen systems, evaluated according to equation (V-22), varied from 0.32 to 1.41, even though all of these systems have large negative second virial coefficients which suggests that these systems are on the verge of precipitation. Elias and Gerber [5D-7] have argued that the initial slope of the Π/ρ_p RT vs. ρ_p curve should not be equated with the second virial coefficient and any interpretation of solution properties based on negative second and positive third coefficients is questionable.

The molecular weight of the PTHF-B1 sample determined in this work is found to be much smaller than indicated by the manufacturer, while the agreement for the molecular weight of PTHF-A2 sample is extremely good (see Tables III and IV). Again, this is suggested to be a result of association. Figure 10 demonstrates how one can be misled with a limited number of data, especially when they cover only a rather narrow concentration range, if the solution under study is an associating system. As indicated by the dotted line in Figure 10, extrapolation of data taken within concentration range 0.20 ~ 0.35 g/dl will yield a polymer molecular weight of 25,000 g/mole for the PTHF-B1 sample, which is identical to the manufacturer's value.

Figure 12 demonstrates the superiority of the

Figure 12. Comparison of Osmotic Pressure Data Fittings Based on Various Solution Theories for PTHF-B1-MEK Solution at 34.0°C.

——— Association Theory of This Work
----- Flory-Huggins Theory


$\frac{\pi}{A_2 \rho RT} \times 10^4$ (mole/g)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0
0
.05
.10
.15
.20
concentration(g/dl)
χ_1= -0.8
$\bar{M}_N$=14,286
χ_1=2.5
$\bar{M}_N$=9,090

association model over the Flory-Huggins theory for associating polymer-solvent mixtures. As can be seen from Figure 12, the one-parameter Flory-Huggins equation (equation (II-12)) cannot fit osmotic pressure data for PTHF-B1-MEK solution. Based on the theory, χ_1 is assigned a value of as high as 2.5 to best fit these data. This is contrary to what the theory predicts that χ_1 should have a maximum value of 0.5.

The idea of associating polymer molecules in solution gains more support from Roßkopf's osmotic pressure data for polyvinylchloride (PVC) solutions [5D-8]. Their results show that the number average molecular weight of their PVC sample, determined by extrapolation of the Π/ρ_p RT vs. ρ_p plot to zero concentration, varies with solvent used and with solution temperature. These results clearly indicate that PVC molecules associate in solution and the degree of association is a function of solvent and temperature.

VI. DIFFUSION IN ASSOCIATING POLYMER SOLUTIONS

A. Thermodynamic Basis of Diffusion in Solution

General diffusion theories normally have been developed either on the basis of a physical model of the diffusion process or using irreversible thermodynamic arguments. The latter approach is adopted here, both to avoid dependence on a possible unrealistic model and because the results are consistent with available kinetic theory and experimental data [6A-1, 2].

The thermodynamic approach is based on three postulates in addition to conservation and symmetry arguments: (a) near equilibrium behavior, (b) linear relations between fluxes and affinities, and (c) microscopic reversibility [6A-3]. The first step in the development of flux relations is to recognize that diffusion is an irreversible process, and thus results in an overall increase on entropy. A quantitative expression for this increase will yield the desired relations between mass fluxes and concentration gradients.

For a n+1 component mixture, it can be shown [6A-4] that:

$$J_S = \frac{q}{T} - \frac{1}{T} \sum_{i=1}^{n+1} \mu_i \; J_i \qquad \text{(VI-1)}$$

where J_S is the overall entropy flux relative to the mass average velocity v_m, q is the total heat flux and J_i the mass flux of species i relative to the mass average velocity. T is the absolute temperature and μ_i the chemical potential of species i. In addition:

$$R_S = -\frac{1}{T} \sum_{i=1}^{n+1} J_i \quad \nabla(\mu_i)_{T,P} \tag{VI-2}$$

where R_S is the volumetric rate of entropy production. Clearly R_S vanishes at thermodynamic equilibrium; that is, when the chemical potential gradients $\nabla(\mu_i)_{T,\,P}$ are zero. The $\nabla(\mu_i)_{T,\,P}$ can then be considered as the "driving forces" for entropy production.

The preceding arguments can be generalized to any "driving forces" or affinities, X_k, and the corresponding "fluxes," F_k, of irreversible processes:

$$R_S = \sum_k K_k \dot{X}_k \tag{VI-3}$$

The second law of thermodynamics requires that the entropy production resulting from all the simultaneous irreversible processes be positive. However, it may happen that a system undergoes simultaneous processes such that:

$$F_j X_j < 0, \text{ while all other } F_i X_i > 0 \ (i \neq j) \tag{VI-4}$$

provided that the sum

$$\sum_k F_k X_k > 0 \tag{VI-5}$$

These irreversible processes are called "coupled processes." Thermodynamic coupling allows one or more of the processes to progress in a direction contrary to hat described by its own affinity. For example, in thermal diffusion, the diffusion of matter against its concentration gradient is accompanied by a negative entropy production, but this effect is compensated by the positive entropy production due to the flow of heat. This example makes it clear that any particular flux in a system depends upon not only its own affinity, but also all other affinities existing in the system.

Thermodynamic considerations alone cannot, however,give the form of the dependence of the fluxes on the driving forces. It is quite natural, at least if the system is close to equilibrium, to assume that each flux is a linear homogeneous function of each driving force:

$$F_i = \sum_j W_{ij} X_j \tag{VI-6}$$

Linear laws of this kind are often called the "phenomenological relations." In addition to being the simplest physically interesting assumption, this relation is consistent with other common flux laws (for example, Newton's law, Fourier's law and Fick's law). Like these relations, it is only a first approximation to real behavior. But also like these others, it is normally a good approximation. The coefficients W_{ij} are called the "phenomenological coefficients," and depend on the state of the system. The coefficient W_{ii} may stand for the heat conductivity or diffusivity, while the coefficients W_{ij} (with $i \neq j$) describe the "interaction" of the two irreversible processes i and j. The phenomenological coefficients have been shown to be symmetric by Onsager on the basis of statistical mechanical arguments [6A-5]; that is:

$$W_{ij} = W_{ji} \qquad \text{(VI-7)}$$

These relations are referred to as the "onsager reciprocal relations," and although their validity is still in some doubt, large deviations form equation (VI-7) are quite unlikely. It should be noted that for the Onsager reciprocal relations to be valid, the J_i and X_i must both be independent [6A-6] (i.e., for a system of n+1 components, there are only n independent J_i and X_i).

Returning to the mass flux problem due to chemical potential gradients $\nabla(\mu_i)_{T,P}$, according to equation (VI-6), one can write for n+1 components:

$$J_i = - \sum_{j=1}^{n} W_{ij} \quad \nabla(\mu_j)_{T,P} \; (i = 1, \text{---} \; n) \qquad \text{(VI-8)}$$

For practical purposes, chemical potential gradients are awkward. Equation (VI-8) can be rewritten in terms of mass fraction gradients. Since

$$\mu_j = \mu_j \; (\omega_1, \; \omega_2, \; \ldots \omega_n, \; T, \; P) \qquad \text{(VI-9)}$$

where ω_i is the mass fraction of component i, therefore

$$\nabla(\mu_j)_{T,P} = \sum_{k=1}^{n} \left(\frac{\partial \mu_j}{\partial \omega_k}\right)_{\substack{\omega_\ell,\ \ell \neq k,n \\ T,P}} \nabla \omega_k \tag{VI-10}$$

Here, component n+1 is chosen as the solvent.

Combining equations (VI-10) and (VI-8), one obtains:

$$\begin{aligned} J_i &= - \sum_{j=1}^{n} W_{ij} \left[\sum_{k=1}^{n} \left(\frac{\partial \mu_j}{\partial \omega_k}\right)_{\substack{\omega_\ell,\, \ell \neq k,n \\ T,P}} \nabla \omega_k \right] \\ &= - \sum_{k=1}^{n} \left[\sum_{j=1}^{n} W_{ij} \left(\frac{\partial \mu_j}{\partial \omega_k}\right)_{\substack{\omega_\ell,\ \ell \neq k,n \\ T,P}} \right] \nabla \omega_k \\ &= - \sum_{j=1}^{n} \rho D^{\omega}_{ik} \nabla \omega_k \\ &= - \rho \sum_{k=1}^{n} D^{\omega}_{ik} \nabla \omega_k \end{aligned} \tag{VI-11}$$

where the generalized Fick's law coefficients are defined by:

$$D^{\omega}_{ik} = \frac{1}{\rho} \sum_{j=1}^{n} W_{ij} \left(\frac{\partial \mu_j}{\partial \omega_k}\right)_{\substack{\omega_\ell,\ \ell \neq k,n \\ T,P}} \tag{VI-12}$$

where ρ is the mass density of the mixture. It can be seen from equation (VI-12) that, in general, $D^{\omega}_{ik} \neq D^{\omega}_{ki}$. If we rewrite equation (VI-10) in terms of mass density gradients:

$$\nabla(\mu_j)_{T,P} = \sum_{k=1}^{n} \left(\frac{\partial \mu_j}{\partial \rho_k}\right)_{\substack{\rho_\ell,\ \ell \neq k,n \\ T,P}} \nabla \rho_k \tag{VI-10'}$$

then

$$J_i = - \sum_{k=1}^{n} D^{\rho}_{ik} \nabla \rho_k \tag{VI-11'}$$

where

$$D^{\rho}_{ik} = \sum_{j=1}^{n} W_{ij} \left(\frac{\partial \mu_j}{\partial \rho_k}\right)_{\substack{\rho_\ell \; \ell \neq k,n \\ T,P}} \tag{VI-12'}$$

The superscripts on diffusivities indicate that their magnitudes depend upon the choice of driving force. It must be noted that in general:

$$D^{\omega}_{ik} \neq D^{\rho}_{ik} \tag{VI-13}$$

In fact,

$$D^{\omega}_{ij} = D^{\rho}_{ij} + \rho\,(\overline{V}_n - \overline{V}_j) \sum_{k=1}^{n} \rho_k D^{\rho}_{ik} \tag{VI-14}$$

where $\overline{V}_i$ is the partial specific volume of species i for mass concentration units. It is the D^{ρ}_{ij} which are normally measured experimentally. It has also been shown [6A-3] that D^{ρ}_{ii} should be always positive, while the "interacting coefficients" may be positive, zero, or negative. In other words, the mass flux of species i could be either accelerated, not affected, or decelerated by driving forces other than its own.

B. Theory of Diffusion in Solutions Containing Associating Polymer Solutes

According to the open association model discussed in Chapter V, an associating polymer solution can be regarded as a multi-component system containing polymer unimer, associated multimers and solvent, instead of a binary system. The associated multimers are assumed to be identical in their chemical properties, but distinguishable in size. It is also assumed that the shape of the multimers is the same as the shape of unimer in solution. Thus, the translational properties of individual unimers and multimers in solution depend primarily on their sizes (as discussed in Chapter II, Part B). The ratio of the concentration of unimer to multimers changes drastically with overall mass concentration of polymer. Therefore, we expect to see the observed diffusion coefficient, which is a measure of diffusion of unimer and multimers, change significantly with overall polymer concentration. The functionality of $D(\rho_P)$ should, of course, depend on the type of association.

Based on the irreversible thermodynamic arguments presented in the previous section, the following set of equations can be written to describe mass flux processes due to concentration gradients existing in an isobaric, isothermal n+1 component system if the "phenomenological laws" are valid:

$$J_1 = - D^*_{11} \nabla\rho_1 - D^*_{12} \nabla\rho_2 - \ldots - D^*_{1n} \nabla\rho_n \qquad \text{(VI-15a)}$$

$$J_2 = - D^*_{21} \nabla\rho_1 - D^*_{22} \nabla\rho_2 - \ldots - D^*_{2n} \nabla\rho_n \qquad \text{(VI-15b)}$$

- -

$$J_n = - D^*_{n1} \nabla\rho_1 - D^*_{n2} \nabla\rho_2 - \ldots - D^*_{nn} \nabla\rho_n \qquad \text{(VI-15n)}$$

where J_i and $\nabla\rho_i$ are mass fluxes and mass concentration gradients of diffusing species i, respectively.

J_1, J_2, ..., etc., are mass fluxes of unimer, dimer, ..., respectively. Component n+1 is chosen as the solvent. Equations (VI-15) are of little use because it is impossible for one to measure separately the mass fluxes of unimer and multimers. The measurable quantity is the overall mass flux, J_{obs}, which is the sum of all mass fluxes J_i. Summing equations (VI-15) gives:

$$\begin{aligned} J_{obs} &= \sum_{i=1}^{n} J_i \\ &= - \left(\sum_{i=1}^{n} D^*_{i1}\right) \nabla\rho_1 - \left(\sum_{i=1}^{n} D^*_{i2}\right) \nabla\rho_2 - \ldots - \left(\sum_{i=1}^{n} D^*_{in}\right)\nabla\rho_n \end{aligned} \qquad \text{(VI-16)}$$

Equation (VI-16) can be written in a more compact form as:

$$J_{obs} = - D_1 \nabla\rho_1 - D_2 \nabla\rho_2 - \ldots - D_n \nabla\rho_n \qquad \text{(VI-17)}$$

where $\left(\sum_{i=1}^{n} D^*_{ij}\right)$ is replaced by D_j.

Since the molar concentration of i-mer C_i is related to the molar concentration of unimer C_1 by:

$$C_i = K^{i-1} C_1^i \qquad \text{(VI-18)}$$

and

$$C_i = \rho_i / \bar{M}_i = \rho_i / i \bar{M}_N \qquad \text{(VI-19)}$$

where ρ_i is the mass concentration of i-mer and $\bar{M}_N$ is the number average molecular weight of unimers, the mass concentration of i-mer can be expressed in terms of mass concentration and number average molecular weight of unimer:

$$\rho_i = \frac{i \bar{M}_N}{K} \left(\frac{K\rho_1}{\bar{M}_N}\right)^i \qquad \text{(VI-20)}$$

Differentiation of equation (VI-20) with respect to unimer mass concentration gives the expression for mass concentration gradient of i-mer:

$$\nabla\rho_i = i^2 \left(\frac{K\rho_1}{\bar{M}_N}\right)^{i-1} \nabla\rho_1 \qquad \text{(VI-21)}$$

Substituting equation (VI-21) into equation (VI-17) yields:

$$J_{obs} = -(D_1 + 4YD_2 + 9Y^2D_3 + \ldots + n^2 Y^{n-1} D_n)\nabla\rho_1 \qquad \text{(VI-22)}$$

where Y is a dimensionless concentration and is defined as

$$Y = \frac{K\rho_1}{\bar{M}_N} \qquad \text{(VI-23)}$$

For non-associating systems, i.e., K=0, Y should be zero, and the unimer concentration would equal the overall concentration. Equation (VI-22) would then reduce to:

$$J_{obs} = D_1 \nabla \rho_1 = - D_{obs} \nabla \rho_P \qquad \text{(VI-24)}$$

as it should for a binary system. Equation (VI-22) cannot be applied directly to interpret experimental results since it is not possible for one to measure either the concentration or concentration gradient of unimer. It is therefore necessary to convert unimer concentration gradient into overall polymer concentration gradient. Since

$$\begin{aligned} \rho_P &= \sum_{i=1}^{n} \rho_i \\ &= (1 + 2Y + 3Y^2 + \ldots + nY^{n-1}) \; \rho_1 \end{aligned} \qquad \text{(VI-25)}$$

therefore

$$\nabla \rho_P = (1 + 4Y + 9Y^2 + \ldots + n^2 \; Y^{n-1}) \; \nabla \rho_1 \qquad \text{(VI-26)}$$

Substitution of equation(VI-26) into equation (VI-22) yields:

$$J_{obs} = \frac{- (D_1 + 4YD_2 + 9Y^2D_3 + \ldots + n^2Y^{n-1}D_n)}{(1 + 4Y + 9Y^2 + \ldots + n^2Y^{n-1})} \; \nabla \rho_P \qquad \text{(VI-27)}$$

Comparing equation (VI-27) to equation (VI-24), it can be seen that:

$$D_{obs} = \frac{(D_1 + 4YD_2 + 9Y^2D_3 + \ldots + n^2Y^{n-1}D_n)}{(1 + 4Y + 9Y^2 + \ldots + n^2Y^{n-1})}$$

$$= \sum_{i=1}^{n} \left(\frac{i^2Y^{i-1}}{\sum_{j=1}^{n} j^2 \; Y^{j-1}}\right) D_i \qquad \text{(VI-28)}$$

Thus, the observed diffusion coefficient is a weighted average of diffusion coefficients of all diffusing species in solution. The weighting factor H_i of the diffusion coefficient D_i is found to be:

$$H_i = \frac{i^2 \; Y^{i-1}}{\sum_{j=1}^{n} j^2 \; Y^{j-1}} \qquad \text{(VI-29)}$$

In general, the diffusion coefficient of i-mer D_i is a function of concentration and can be expressed as:

$$D_i = D_i^0(1 + k_d^{(i)} \; \rho_P + \ldots) \qquad \text{(VI-30)}$$

where D_i^0 is the limiting diffusion coefficient of i-mer at zero concentration and $k_d^{(i)}$ the concentration dependence constant of D_i. Substitution of equation (VI-30) into equation (VI-28) gives:

$$D_{obs} = \sum_{i=1}^{n} \left(\frac{i^2 \; Y^{i-1}}{\sum_{j=1}^{n} j^2 \; Y^{j-1}}\right) D_i^0 \; (1 + k_d^{(i)} \; \rho_p + \text{---} \;) \qquad \text{(VI-31)}$$

Both experimental results [6B-1, 2] and theoretical prediction (see Chapter II, part B) have shown that the limiting diffusion coefficient is inversely proportional to the molecular weight of the diffusing molecule by the relation:

$$D_i^0 = G\ M_i^{-a} \qquad \text{(VI-32)}$$

Elias [6B-3] showed that the parameter a should satisfy the equation:

$$a = (1 + \gamma)/3 \qquad \text{(VI-33)}$$

in which γ is defined by the relation:

$$[\eta]_i = K_v\ \overline{M}_i^{\gamma} \qquad \text{(VI-34)}$$

Normally, γ ranges from 0.5 for a theta solvent to 0.8 for a good solvent. Therefore, the parameter a should range from 0.5 to 0.6. For systems in which association between polymer molecules is significant, the so-called "excluded volume effect" is expected to be minimal and the parameter a can be approximated by 0.5. Thus:

$$\frac{D_i^0}{D_1^0} = \left(\frac{\overline{M}_i}{\overline{M}_N}\right)^{-\frac{1}{2}} = \left(\frac{i\ \overline{M}_N}{\overline{M}_N}\right)^{-\frac{1}{2}} = i^{-\frac{1}{2}} \qquad \text{(VI-35)}$$

Substituting equation (VI-35) into equation (VI-31) gives:

$$D_{obs} = D_1^0 \sum_{i=1}^{n} \left(\frac{i^{1.5} Y^{i-1}}{\sum_{j=1}^{n} j^2 Y^{j-1}} \right) (1 + k_d^{(i)} \rho_P + ---)$$

$$= D_1^0 \sum_{i=1}^{n} B_i (1 + k_d^{(i)} \rho_P + ---) \qquad (VI\text{-}36)$$

where

$$B_i \equiv \frac{i^{1.5} Y^{i-1}}{\sum_{j=1}^{n} j^2 Y^{j-1}} \qquad (VI\text{-}37)$$

Equation (VI-36) can be further reduced to:

$$D_{obs} = D_1^0 \left[\sum_{i=1}^{n} B_i + \sum_{i=1}^{n} B_i k_d^{(i)} \rho_P + --- \right]$$

$$= D_1^0 \left(\sum_{i=1}^{n} B_i \right) \left[1 + \frac{\sum_{i=1}^{n} B_i k_d^{(i)}}{\sum_{i=1}^{n} B_i} \rho_P + --- \right] \qquad (VI\text{-}38)$$

Equation (VI-38) can be rewritten in a simpler form as:

$$D_{obs} = D^0 \chi_{asso} (1 + k_d^m \rho_P + ---) \qquad (VI\text{-}39)$$

where

$$\chi_{asso} = \sum_{i=1}^{n} B_i = \sum_{i=1}^{n} \frac{i^{1.5} Y^{i-1}}{\sum_{j=1}^{n} j^2 Y^{j-1}} \qquad (VI\text{-}40)$$

and the parameter k_d^m can be regarded as the linear concentration dependence constant of the average diffusion coefficient of all diffusing associated and non-associated species. k_d^m is caused by thermodynamic and hydrodynamic interactions as well as by association effects. It should be noed that in equation (VI-39) D_1^0 has been replaced by D^0 because significant association between polymer molecules at infinite dilution is most unlikely and therefore there should be no difference between D^0 and D_1^0. The association term in equation (VI-39) is a decreasing function of concentration. It decreases sharply in the infinitely dilute region and gradually levels off. This is illustrated by Figure 13. In general, the association term dominates in the infinitely dilute region, while the intermolecular thermodynamic- and hydrodynamic-interaction term $(1 + k_d^m \rho_P + ---)$ becomes important at higher concentrations. It is noteworthy that for non-associating systems, Y is zero, $\chi_{asso} = 1.0$, and equation (VI-39) can be reduced to:

$$D_{obs} = D^0(1 + k_d \rho_P + ---) \tag{VI-41}$$

as expected. According to equation (VI-25):

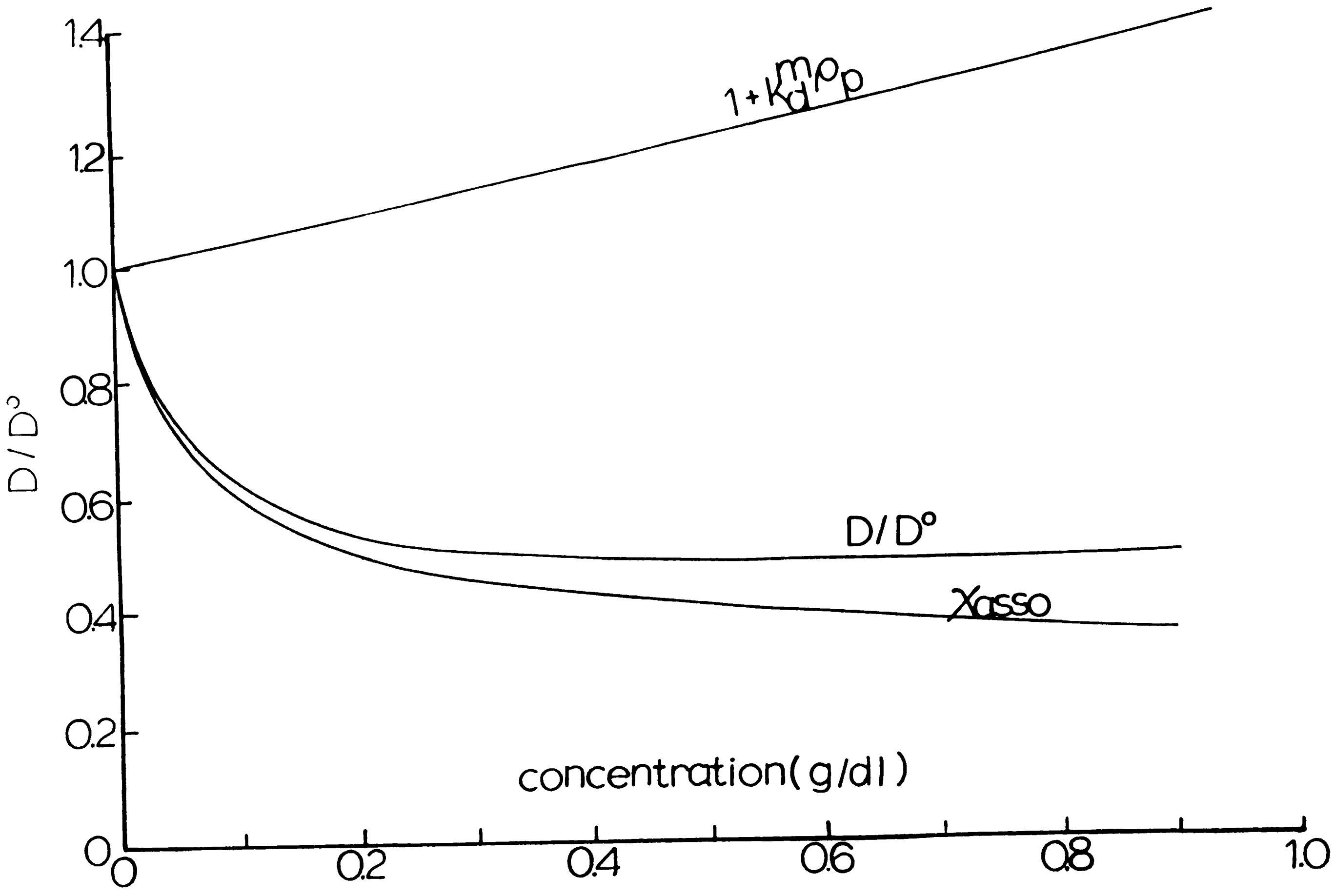
$$X \equiv \frac{K\rho_P}{\overline{M}_N} = \frac{Y}{(1 - Y)^2} \tag{VI-42}$$

or

$$Y = \frac{(1 + 2X) - (1 + 4X)^{\frac{1}{2}}}{2X} \tag{VI-43}$$

The other root of Y is rejected since it violates the constraint that Y has to be less than 1.0 (see Chapter V,

Figure 13. Sample Calculation of Concentration Dependence of D/D^0, χ_{asso} and $(1+k_d^m \rho_P+ ---)$.
$D = D^0 \chi_{asso} (1+k_d^m \rho_P + ---)$.



1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
D / D°
$1+K_d^m \rho_p$
D/D°
χ_{asso}
concentration(g/dl)
0
0.2
0.4
0.6
0.8
1.0

part C).

Equation (VI-40) and (VI-43) enable one to calculate χ_{asso} as a function of overall polymer mass concentration providing prerequisite knowledge of the association equilibrium constant K and the true number average molecular weight of the polymer sample $\overline{M}_N$ are known. In practice, K and $\overline{M}_N$ can be determined from osmotic pressure and/or light scattering data. Equation (VI-36) also provides a method for determining D^c of associating polymer solutions.

C. Presentation of Interferometry Diffusion and Discussions

Figures 14, 15, 16 show the concentration dependence of diffusion coefficients of various PTHF-solvent systems. For non-associating systems (containing polymer with CH_3 end-groups) linear extrapolations were applied to determine D^0 and k_d. For associating systems (containing polymer with OH end-groups) equation (VI-39) was applied (using a least square technique) to fit the experimental data. The results are also summerized in Table V. The concentration dependence constant (k_d) increases with polymer molecular weight in both non-associating PRHF-MEK and PTHF-BB systems (see Figure 14). This finding indicates, according to the thermodynamic- hydrodynamic-interaction arguments of the non-associating polymer solution theory (i.e., equation (II-71)), that the increase of molecular weight of diffusing polymer molecules has stronger effect on improving the driving force than on increasing the frictional force.

Equation (VI-37) for associating systems predicts that the diffusion coefficient should increase sharply with decreasing concentration near the zero concentration intercept. This is due to the reduction of the average size of diffusing polymer molecules as a result of dissociation of polymer multimers accompanied with dilution process. The data for the four associating polymer mixture are shown on Figures 15 and 16, along with the expected extrapolations according to the theory. Although the interferometric

Figure 14. Concentration Dependence of Diffusion Coefficients of Non-Associating PTHF Solutions at 34.0°C.

PTHF-A1 in MEK--○ ;
PTHF-A1 in BB---△ ;
PTHF-A2 in MEK--▲ ;
PTHF-A2 in BB---● .

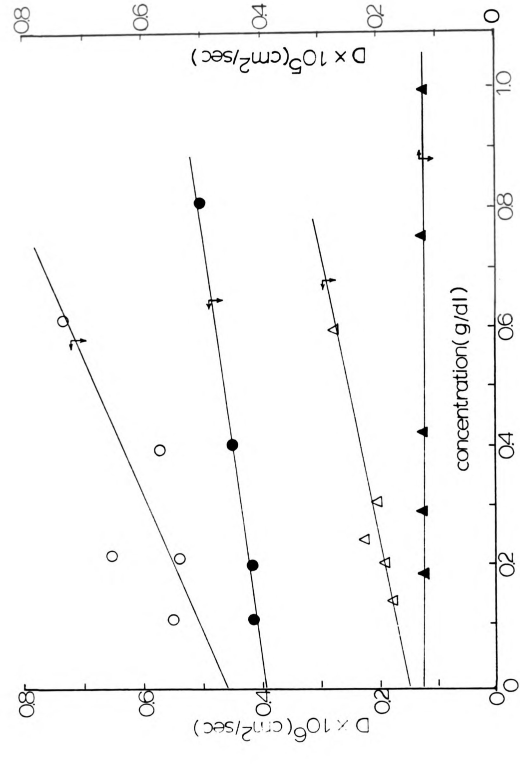

D × 10^6 (cm^2/sec)
0.8
0.6
0.4
0.2
0
D × 10^5 (cm^2/sec)
0.8
0.6
0.4
0.2
0
concentration (g/dl)
0
0.2
0.4
0.6
0.8
1.0

Figure 15. Concentration Dependence of Diffusion Coefficients of Associating PTHF-MEK Solutions at 34.0°C.

PTHF-B1 in MEK--● ;
PTHF-B2 in MEK--○ .

(The curves were determined based on equation (VI-39) using least square tehcnique.)

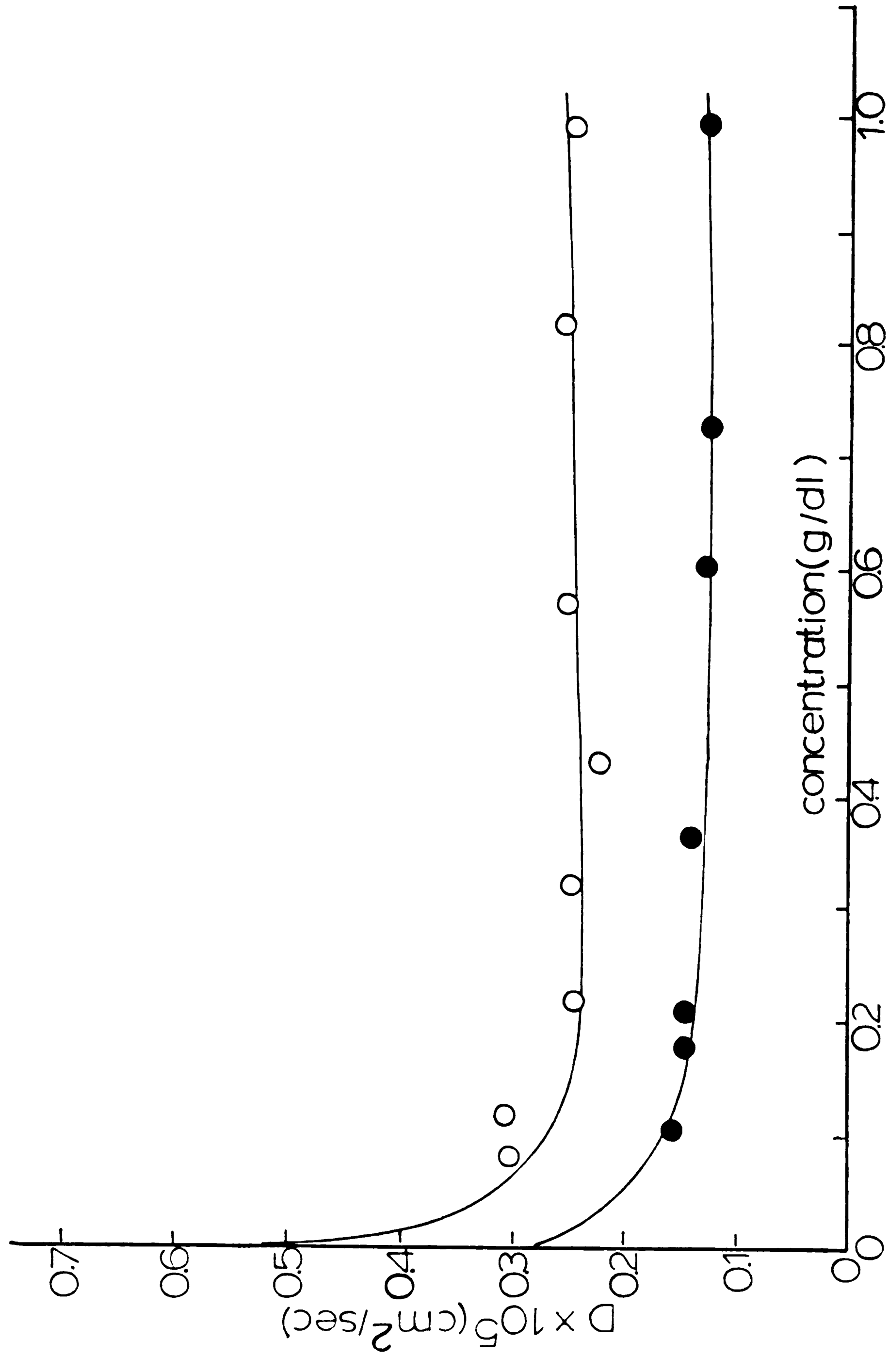

D x 10⁵ (cm²/sec)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
0.2
0.4
0.6
0.8
1.0
concentration(g/dl)

Figure 16. Concentration Dependence of Diffusion Coefficients of Associating PTHF-BB Solutions at 34.0°C.

PTHF-B1 in BB--▼;
PTHF-B2 in BB--△.

(The curves were determined based on equation (VI-39) using least square technique.)

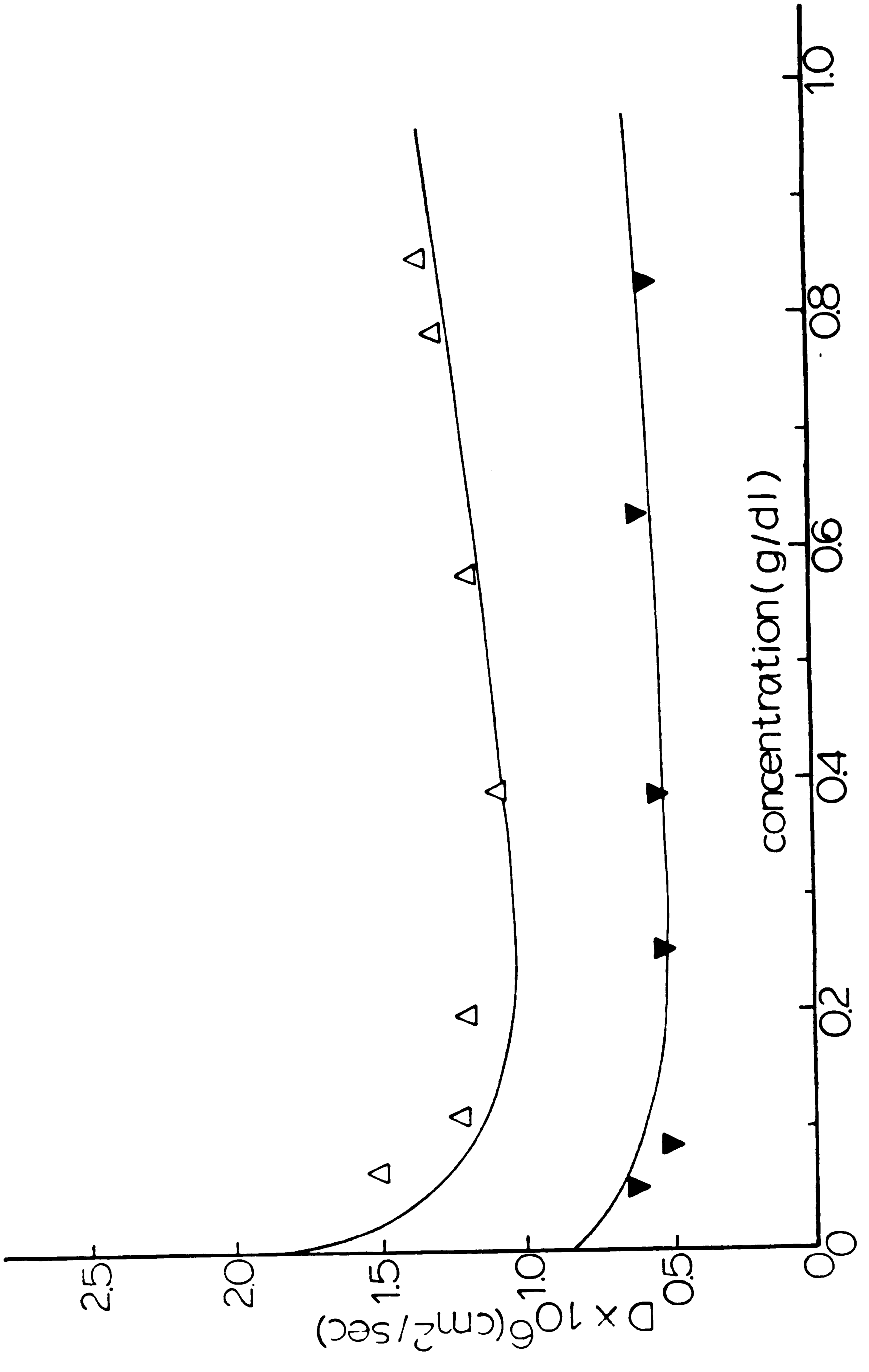

D × 10^6 (cm^2/sec)
0.0
0.5
1.0
1.5
2.0
2.5
0.0
0.2
0.4
0.6
0.8
1.0
concentration (g/dl)

Table V. Summary of Diffusion Coefficient Data for PTHF-Solvent Systems at 34.0°C.

Polymer Solute-Solvent	$K/\overline{M}_N \times 10^{-4}$ (cc/gm)	$D^0 \times 10^6$ (cm^2/sec) (Experimental)*	$D^0 \times 10^6$(cm^2/sec) (Predicted by Fedors' Relation)	Percentage Deviation	k_d(or k_d^m) 10^{-2} (cc/gm)
A1-MEK	---	0.4643	0.4444	4.286	0.9176
A2-MEK	---	1.2710	1.3600	- 7.002	-0.0933
B1-MEK	0.140	2.7190	2.6914	1.015	0.4253
B2-MEK	0.428	5.2000	4.7110	9.404	1.3710
A1-BB	---	0.1516	0.1745	-15.106	1.2970
A2-BB	---	0.3936	0.5339	-35.645	0.3417
B1-BB	0.065	0.8009	1.0567	-31.939	0.8009
B2-BB	0.200	1.8250	1.8496	- 1.348	1.3190
			Root Mean Square Deviation	16.687	

*The experimental D^0 values of associating PTHF-solvent systems were determined according to the association theory (equation VI-39) and those of non-associating PTHF-solvent systems were determined by linear extrapolation (equation II-70).

method will not provide data at low enough concentration in all cases, the data clearly indicate increased diffusion coefficients at lower concentrations.

As it has been shown by Figure 13, the association theory predicts that the effect of association on diffusion rate becomes much less significant at higher concentrations than it is in the infinitely dilute region. For the four associating PTHF-solvent systems, however, the remaining not-so-significant association effect at higher concentration seems to compensate other effects and, as a result, the diffusion rate is found to be independent of polymer concentration within this concentration region (see Figures 14 and 15). Equation (II-70) and (II-71) of the non-association theory are not able to describe the complex nature of the diffusional property of associating polymer-solvent mixtures.

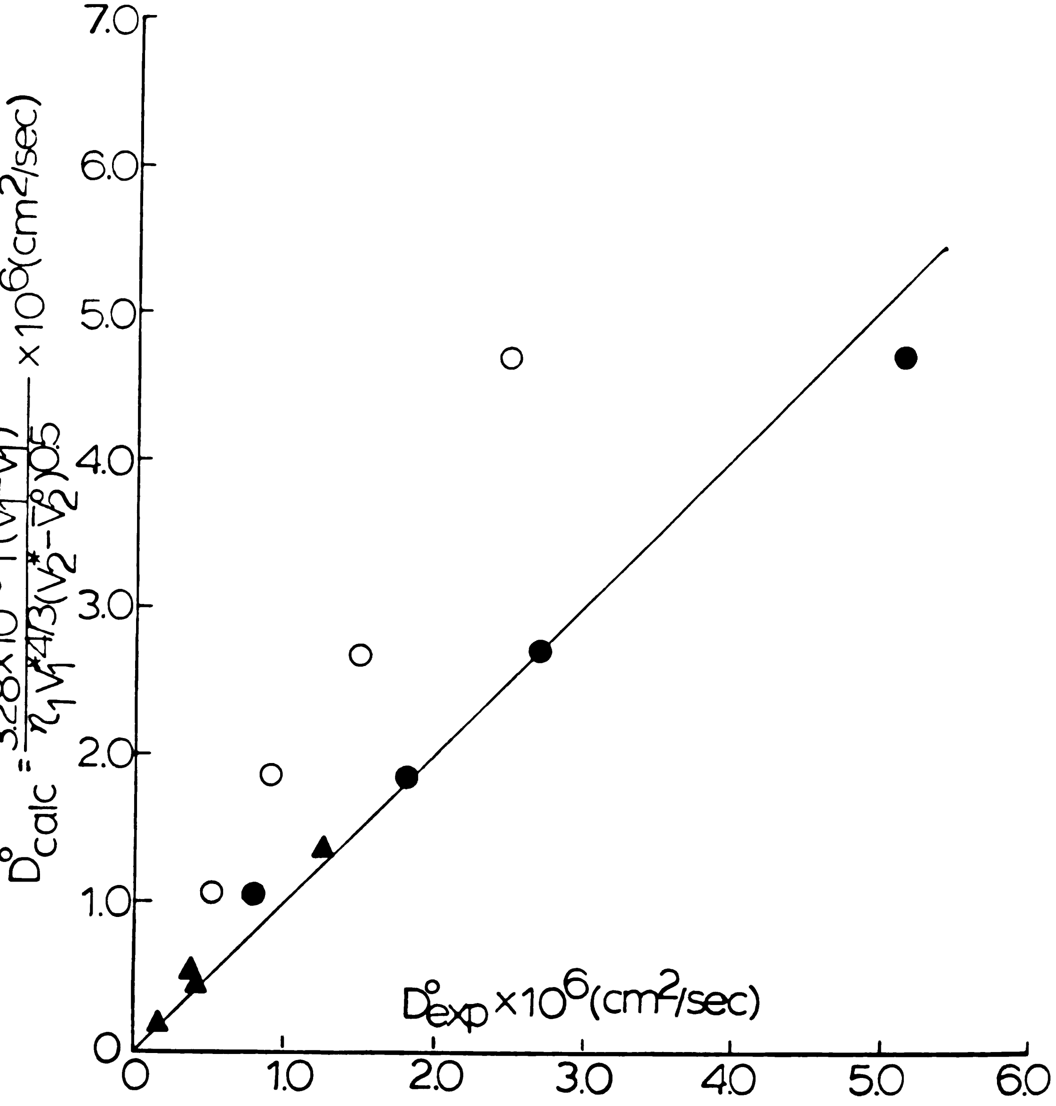
Scattered evidences on associating systems seemed to indicate that the association of polymer molecules is restricted to very peculiar polymer/solvent/temperature combinations. This might not be true. The association theory projects that there exists a very narrow range of effective association strength $K/\overline{M}_N$ within which the association of polymer molecules is detectable. For low $K/\overline{M}_N$, the association effect would be insignificant compared to other interactions. On the other hand, if $K/\overline{M}_N$ is high, the association process would be complete at such low concentrations that accurate diffusion measurements are not possible. The latter is exactly the case for the four systems under study. In fact, without the osmotic pressure data which provide clear evidence of polymer molecular association, one would likely fit the diffusion data of these four systems with a non-association model. It is therefore concluded that the interferometry method of diffusion coefficient measurements is not a good choice for detecting intermolecular association.

The finding that the diffusion coefficient increases sharply with decreasing polymer concentration in dilute associating polymer solutions casts doubt on the reliability of some D^0 values reported in the literature, since these values have been obtained by linear extrapolation. This might also explain the lack of agreement between D^0 values observed in some laboratories and those predicted by theoretical considerations. Unfortunately, accurate measurements of diffusion coefficients in the infinitely dilute region is difficult (or impossible in some cases) by using traditional apparatus. The association phenomena might therefore be overlooked. In Figure 15 and 16, only limited evidence shows that the $D(\rho_p)$ curves shall increase with decreasing polymer concentration. In order to support the association arguments, therefore, it is worthwhile and also interesting to compare the D^0 values of these associating systems determined from the association model with corresponding D^0 values predicted by existing theories. Fedors' empirical relation, presented in Chapter II, part B, was chosen for this purpose because it needs no extra experimental data besides the viscosity of the solvent and is the easiest method to apply. It can be seen from Figure 17 that the Fedors' relation correlates D^0 data of all eight PTHF-solvent systems satisfactorily (see also Table V) if D^0 values of associating systems were determined according to the associating model. It should be mentioned, however, the constant parameter on the right hand side of equation (II-69) was determined to be 3.28×10^{-9} (using a least square technique), instead of 4.5×10^{-9}, for the best correlation. More reliable data will be needed to confirm the exact value for the parameter. The distance between open circles and the 45° line in Figure 17 shows the deviation of D^0 values of the four associating systems, if they were determined by linear extrapolation, from Fedors' prediction. This illustration provides good explanation for the observation that the predicted D^0 values are higher than they were determined in the laboratory in some systems [6C-1, 2].

It is interesting to point out that the limiting diffusion coefficient D^0 of the four associating systems under study, when determined according to the association model, have values about 1.5 to 2.0 times as much as they will be if the non-association model was to be applied. This might explain the finding reported by a number of investigators that a "unimer-trimer" [6C-1] or a "unimer-

Figure 17. Correlations Between Experimental D° Values of PTHF-Solvent Systems and Fedors' Empirical Relation.

Non-associating systems--------- ▲
Associating systems (determined according to association model)------------ ●
Associating systems (determined by linear extrapolation)--------------- ○


$D^{\circ}_{calc} = \frac{3.28\times10^{-9}\,T(V_1^{*}-V_1)^{1.5}}{\eta_1 V_1^{*4/3}(V_2^{*}-\bar{V}_2^{\circ})^{0.5}} \times 10^{6}$ (cm²/sec)
$D^{\circ}_{exp} \times 10^{6}$ (cm²/sec)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0
1.0
2.0
3.0
4.0
5.0
6.0

tetramer" [6C-2] model interpreted their diffusion data reasonably well.

VII. CONCLUSIONS AND RECOMMENDATIONS

An association model is presented which provides an explanation for some conflicts between experimental observations and existing thermodynamics and diffusion theories of non-associating systems. The osmotic pressure equation derived in Chapter IV based on the association model is found to be analogous to the van der Waals equation, not only in form, but also in the physical meaning of the corresponding parameters. This result is hardly surprising considering the similarities between the two systems. The diffusion equation based on the association model predicts that for associating polymer-solvent systems, the diffusion coefficient should first decrease with increasing polymer concentration and then increase slightly, remain constant, or decrease slowly with concentration, depending on the sign of the intermolecular interaction parameter k_d^m. This prediction is consistent with experimental observations. It is worthwhile to point out that both osmotic pressures and diffusion data from this work were found to fit the association model very well, and more importantly, the association constant K and the number average molecular weight $\overline{M}_N$ determined from different measurements are in good agreement, indicating that the association model is self-consistent.

The following recommendations are proposed for further work:

(1) Data should be obtained for polymer samples with identical structures and average molecular weights, but with different functional end-groups. The purpose would be to elucidate the effects of association upon thermodynamic and transport properties in polymer solutions. A family of $\Pi/\rho_p RT$ vs. ρ_p curves of such polymer-solvent systems should provide an excellent test of predictions made by the association model. Polymer molecules would be expected to associate to a different extent in the same solvent if they have different functional end-groups. Therefore $D(\rho_p)$ curves of such systems should be similar in their shapes, but different in magnitudes. However, these systems should have identical D^0.

(2) Obtain experimental data for trace-diffusion coefficients of the polymer samples in the same solvents. The advantages of this are:

   (a) To overcome the difficulty in obtaining accurate diffusion coefficients in the dilute concentration region. Tracer diffusion coefficients must extrapolate to the mutual diffusion coefficients at infinite dilution, and tracer coefficients should be measurable at much lower concentrations.

(b) To determine the limiting diffusion coefficient D^0 with greater accuracy to justify existing theories for the estimation of D^0.

(c) To test the validity of the association model proposed in this work. Although the model fits the data from this work, as well as from the literature with good results, more systematic data are needed to test the model more extensively.

NOMENCLATURE

NOMENCLATURE

A_i	Species i (equations (V-1) and (V-2))
A_i	the ith virial coefficient
A_i^*	the ith virial coefficient of associating polymer solutions
$(A_i)_{obs}$	observed ith virial coefficient defined by equations (V-31) and (V-32)
a	van der Walls parameter defined by equation (V-27)
a	parameter defined by equation (VI-32)
a'	parameter defined by equations (V-59) and (V-60)
$\bar{a}$	effective bond length (equation (II-43))
B	molar excluded volume defined by equation (V-29)
b	van der Waals parameter defined by equation (V-27)
b_1	parameter defined by equation (II-72)
C_i	molar concentration of i-mer
C_P	true molar concentration of polymer defined by equation (V-5)
C_P	configurational heat capacity of solvent defined by equation (II-29)
3c	total number of external degrees of freedom of a polymer molecule
c/q	structural factor of pure polymer melt
c/r	structural factor of pure polymer melt
<c/q>	average structural factor of a mixture
D_{11}	self-diffusion coefficient
D^0	limiting diffusion coefficient at infinite dilution
D_i	diffusion coefficient of component i (or i-mer) in a multi-component system

D_{obs}	observed diffusion coefficient of an associating polymer solution
D_{ij}	diffusion coefficient defined by equations (VI-12) and (VI-12')
ΔE_i^v	molar energy of vaporization of component i
F_k	flux of irreversible process k
f^0	frictional coefficient at infinite dilution
G	parameter defined by equation (VI-32)
ΔG_m	free energy of mixing
g	constant defined by equation (V-22)
H_i	weighting factor of diffusion coefficient of i-mer
ΔH_m	enthalpy of mixing
$\overline{\Delta H_1}$	partial enthalpy of solvent
h(z)	function defined by equation (II-49)
J_s	entropy flux relative to the mass average velocity
J_i	mass flux of species i (or i-mer) relative to mass average velocity
J_{obs}	observed mass flux
K	association equilibrium constant defined by equations (V-1) and (V-3) (open association)
K_c	association equilibrium constant defined by equation (V-2) (closed association)
k	Boltzmann's constant
k_1	enthalpic parameter defined by equation (II-16)
k_d	parameter defined by equation (II-70)
k_s	parameter defined by equation (II-73)
$k_d^{(i)}$	parameter defined by equation (VI-30)
k_d^m	parameter defined by equation (VI-39)

k_f	parameter defined by equation (II-59)
k_v	parameter defined by equation (II-54)
M	average molecular weight of polymer
$\overline{M}_I$	number average molecular weight of unimers; true number average molecular weight (= $\overline{M}_N$)
$\overline{M}_N$	number average molecular weight of polymer
$(\overline{M}_N)_{app, \theta}$	apparent number average molecular weight of polymer molecules in associating solutions under theta condition
$\overline{M}_v$	viscosity average molecular weight of polymer
$\overline{M}_n$	number average molecular weight of n-mer in an associating polymer solution
N_A	Avagadro's number
n	refractive index (equation IV-3))
n	number of segments in a polymer chain
n_i	number of moles in component i
P	universal constant defined by equation (II-55)
P^*	characteristic pressure defined by equations (II-21) and (II-24)
$\langle P^* \rangle$	average characteristic pressure of a mixture
q	heat flux (equation (VI-1))
qZ	number of external contacts of a polymer chain
R	universal gas constant
$\langle R^2 \rangle$	mean-square end-to-end distance
$\langle R^2 \rangle_0$	unperturbed mean-square end-to-end distance
R_e	radius defined by equation (II-62)
R_f	radius of a non-free-draining pseudo-spherical polymer molecule
R_S	volumetric rate of entropy production

r	ratio of partial molar volume of polymer to that of solvent
$\langle S^2 \rangle$	mean-square radius of gyration
$\overline{\Delta S_1}$	partial entropy of solvent in solution
ΔS_m	entropy of mixing
T	absolute temperature
T^*	characteristic temperature defined by equations (II-21) and (II-24)
$\langle T^* \rangle$	average characteristic temperature of a mixture
t	time
$-U$	energy of vaporization of solvent
$\underline{u}$	excluded-volume per polymer molecule
$\underline{V}$	mean volume occupied by a polymer molecule in solution defined by equation (V-21)
V_i	molar volume of component i
$\overline{V}_i^0$	partial molar volume of component i at infinite dilution
V_i^*	molar volume of component i at its critical temperature
ΔV_m	volume change of mixing
v	molar volume of van der Waals gas
v_m	mass average velocity
W_{ij}	phenomenological coefficient defined by equation (VI-6)
Δw	interchange free energy defined by equation (II-5)
Δw_H	enthalpic interchange energy (equation (II-11))
Δw_S	entropic interchange energy (equation (II-11))
X	frictional parameter defined by equation (II-51)
X	dimensionless concentration defined by equation (VI-42)

X_i	surface fraction of component i
X_k	affinity of irreversible process k
Y	dimensionless concentration defined by equation (VI-23)
Z	coordinate number
z	excluded-volume parameter defined by equation (II-43)
α	degree of association defined by equation (V-15)
α_R	expansion factor defined by equation (II-46)
α_S	expansion factor defined by equation (II-47)
β	binary cluster integral
β	empirical constant defined by equation (II-36)
γ	parameter defined by equation (II-54)
$\bar{\delta}$	parameter of cohesive energy difference between solute and solvent molecules defined by equation (II-32)
δ_i	square root of cohesive energy density of component i defined by equation (II-37)
$\delta_{i,np}$	non-polar part of δ_i defined by equation (II-40)
$\delta_{i,p}$	polar part of δ_i defined by equation (II-40)
$\delta_{i,H}$	hydrogen bonding contribution to δ_i defined by equation (II-40)
η_0	viscosity of solvent
$[\eta]$	intrinsic viscosity of a mixture
θ	theta temperature; a characteristic parameter of polymer solution defined by equation (II-18)
μ_1	chemical potential of solvent in solution
μ_1^0	chemical potential of pure solvent
ν	parameter defined by equation (II-31)
Π	osmotic pressure

τ	parameter defined by equation (II-30)
ρ	mass density
ρ_P	polymer mass concentration
$\bar{\rho}$	parameter defined by equation (II-33)
ρ_k	mass concentration of component k
ϕ_i	volume fraction of component i
ω_i	mass fraction of component i
ε_{ij}	contact (potential) energy between molecules i and j
Ψ_1	entropic parameter defined by equation (II-16)
d	distance between two interacting molecules (polymer segments)
ψ	universal function of potential energy of a pair of molecules
χ_1	interaction parameter defined by equation (II-8) (dimensionless)
χ_{asso}	parameter defined by equation (VI-40)
χ_H	enthalpic interaction parameter (equation (II-11))
χ_S	entropic interaction parameter (equation (II-11))
ζ	frictional coefficient of a polymer segment in solution
Φ	universal constant defined by equation (II-56)

APPENDICES

APPENDIX A

Sample Calculation for the Determination of Diffusion Coefficient

Polymer: PTHF-A2 ($\overline{M}_N$ = 30,000)

Solvent: methyl-ethyl-ketone

Solution I (for the upper level of diffusion cell)
Concentration = 0.8474 g/dl

Solution II (for the lower level of diffusion cell)
Concentration = 1.1464 g/dl

Photographic Plate:

Exposure Number	Time (seconds)
1	0
2	720
3	1440
4	2160
5	2880
6	3600

Total number of fringes: J = 14.6

j	$(x'_o - x'_j)$(cm)	k	$(x'_o + x'_k)$(cm)	$((x'_o + x'_j) - (x'_o - x'_j))$(cm)
Exposure 1				
4	0.9896	8	1.1257	0.1361
5	1.0272	9	1.1580	0.1308
6	1.0625	10	1.1898	0.1273
Exposure 2				
4	0.9762	8	1.1235	0.1473
5	1.0163	9	1.1581	1.1418
6	1.0539	10	1.1933	0.1394
Exposure 3				
4	0.9605	8	1.1183	0.1578
5	1.0036	9	1.1555	0.1519
6	1.0429	10	1.1925	0.1496
Exposure 4				
4	0.9435	8	1.1122	0.1687
5	0.9892	9	1.1511	0.1619
6	1.0316	10	1.1908	0.1592
Exposure 5				
4	0.9283	8	1.1065	0.1782
5	0.9766	9	1.1475	0.1709
6	1.0231	10	1.1897	0.1666
Exposure 6				
4	0.9138	8	1.1010	0.1872
5	0.9648	9	1.1455	0.1807
6	1.0136	10	1.1893	0.1757

j	$\frac{J - 2j}{J}$	A $\mathrm{erf}^{-1}(\frac{J - 2j}{J})$	k	$\frac{2k - J}{J}$	B $\mathrm{erf}^{-1}(\frac{2k - J}{J})$	$\frac{1}{A + B}$
4	0.45205	0.42486	8	0.09589	0.08519	1.96059
5	0.31507	0.28691	9	0.23288	0.20941	2.01483
6	0.17808	0.15916	10	0.36986	0.34050	2.00136

$(x'_k + x'_j)$ (cm)		$\frac{(x'_k + x'_j)^2}{(A + B)^2}$ (cm^2)
Exposure 1		
0.1361		0.0713
0.1308		0.0695
0.1273		0.0649
	Average:	0.0685
Exposure 2		
0.1473		0.0835
0.1418		0.0816
0.1394		0.0778
	Average:	0.0810
Exposure 3		
0.1578		0.0958
0.1519		0.0937
0.1496		0.0896
	Average:	0.0930

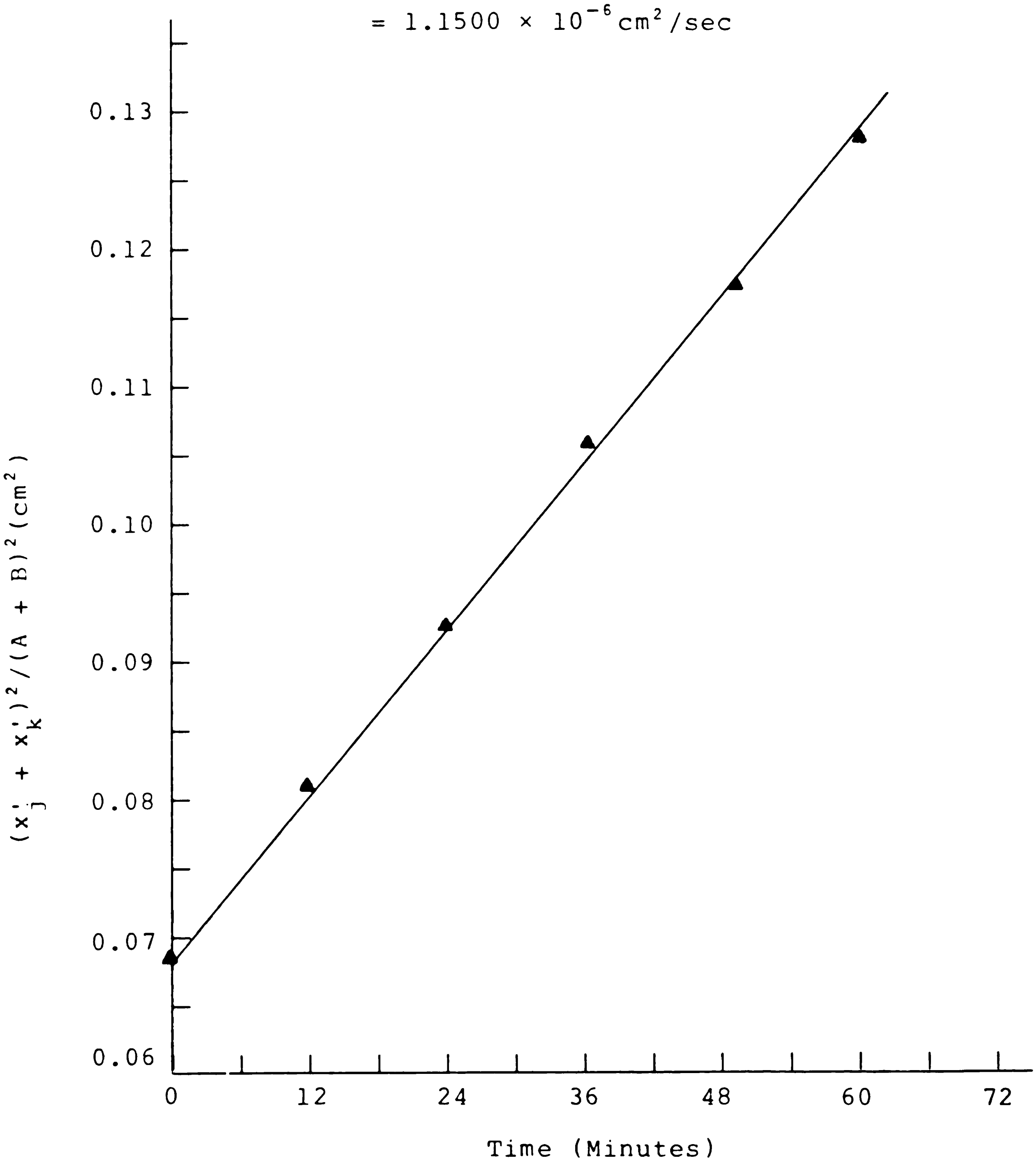
$(x'_k + x'_j)$ (cm)		$\frac{(x'_k + x'_j)^2}{(A + B)^2}$ (cm^2)
Exposure 4		
0.1687		0.1093
0.1619		0.3262
0.1592		0.1015
	Average:	0.1058
Exposure 5		
0.1782		0.1221
0.1709		0.1186
0.1666		0.1111
	Average:	0.1173
Exposure 6		
0.1872		0.1347
0.1807		0.1318
0.1757		0.1237
	Average:	0.1301

Slope of the plot = 1.7117×10^{-5} cm^2/sec

Diffusivity = Slope/4M^2

$= 1.7117 \times 10^{-5}/14.884$

$= 1.1500 \times 10^{-6}$ cm^2/sec



APPENDIX B

Diffusion Data from Interferometry

Polymer	Solvent	Concentration (g/dl)	D × 10^6 (cm^2/sec)
PTHF-A1	MEK	0.1031	0.5547
		0.2045	0.5450
		0.2126	0.6551
		0.3892	0.5718
		0.6089	0.7346
PTHF-A2	MEK	0.1806	1.1940
		0.2902	1.2290
		0.4237	1.2320
		0.7541	1.1870
		0.9969	1.1500
PTHF-B1	MEK	0.1029	1.5830
		0.1759	1.4890
		0.2069	1.5010
		0.3632	1.4560
		0.6051	1.3330
		0.7286	1.3000
		0.9942	1.3590
PTHF-B2	MEK	0.0792	3.023
		0.1128	3.098
		0.2150	2.508
		0.3203	2.503
		0.4279	2.273
		0.5721	2.563
		0.8197	2.613
		0.9920	2.548
PTHF-A1	BB	0.135	0.1732
		0.202	0.1866
		0.239	0.2210
		0.303	0.1986
		0.593	0.2687
PTHF-A2	BB	0.105	0.415
		0.196	0.416
		0.400	0.448
		0.806	0.502

Polymer	Solvent	Concentration (g/dl)	$D \times 10^6$ (cm^2/sec)
PTHF-B1	BB	0.0500	0.597
		0.0825	0.502
		0.2510	0.5210
		0.3875	0.5420
		0.6270	0.6020
		0.8235	0.5520
PTHF-B2	BB	0.062	1.486
		0.113	1.213
		0.196	1.183
		0.391	1.060
		0.574	1.165
		0.785	1.268
		0.847	1.306

BIBLIOGRAPHY

BIBLIOGRAPHY

(1A-1) J.S. Vrentas and J.L. Duda, *J. Appl. Polym. Sci.*, *20*, 2569 (1967)

(1A-2) K. Raju and R.F. Blanks, *J. Polym. Sci., Polym. Phys. Ed.*, *17*, 583 (1979)

(1A-3) J.P. Kratohvil, *Chem. Phys.* Letters, *60*, 238 (1979)

(1A-4) A.F. Schick and S.J. Singer, *J. Phys. Chem.*, *54*, 1028 (1950)

(1A-5) N. Yamada, N. Yokouchi, H. Sato and R. Nakamura, *Reports on Progress in Polymer Physics in Japan*, *8* 27 (1965)

(1A-6) A.M. Afifi-Effat and J.N. Hay, *J. Polym. Sci.*, Part B, *9* 651 (1971)

(1A-7) H. Staudinger, *Die Hochmolekularen Organischen Verbindunger*, Springer, Berlin (1932)

(1A-8) P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York (1953); M.L. Huggins, *Physical Chemistry of High Polymers*, John Wiley & Sons, Inc., New York (1958)

(2A-1) J.H. Hildebrand and S.E. Wood, *J. Chem. Phys.*, *1*, 817 (1933)

(2A-2) J.H. Hildebrand and R.L. Scott, *Regular Solutions*, Prentice-Hall Inc., Englewood Cliffs, New Jersey, Ch. 3 (1962).

(2A-3) P.J. Flory, *Principles of Polymer Chemistry*, Cornell Universtiy Press, New York (1953)

(2A-4) M.L. Huggins, *Physical Chemistry of High Polymers*, John Wiley & Sons, Inc., New York, Ch. 6 (1958)

(2A-5) E.A. Guggenheim, Discussions Faraday Soc., 15, 24 (1953)

(2A-6) D. Patterson, Macromolecules, 4, 30 (1971)

(2A-7) I. Prigogine, A. Bellemans and V. Mathot, The Molecular Theory of Solutions, North-Holland, Amsterdam, Ch. 16 and Ch. 17 (1957)

(2A-8) D. Patterson, Rubber Chem. & Tech., 40, No. 1, 1 (1967)

(2A-9) D. Patterson, J. Polym. Sci., Part C, 16, 3379 (1968)

(2A-10) R. Simha and A.J. Havlik, J. Am. Chem. Soc., 86 197 (1964)

(2A-11) J.H. Hildebrand and R.L. Scott, Solubility of Non-Electrolytes, Reinhold, New York (1950); (a) chapter 7, (b) chapter 20.

(2A-12) R.F. Blanks and J.M. Prausnitz, I & EC Fundamentals, 3, No. 1, 1 (1964)

(2A-13) C.M. Hansen, K. Skaarup, J. Paint Tech., 39, No. 511, 505 (1967)

(2A-14) J. Brandrup, E.H. Immergut and W. McDowell, Polymer Handbook, John Wiley & Sons, New York (1975)

(2A-15) E.A. Guggenheim, Proc. Roy. Soc., A183, 203 (1944)

(2A-16) D. Patterson, Rubber Chem. & Tech., 40, No. 1, 1 (1967)

(2A-17) J. Biros, L. Zeman and D. Patterson, Macromolecules, 4, No. 1, 30 (1971)

(2A-18) H. Yamakawa, Modern Theory of Polymer Solutions, Harper and Row Publishers, New York (1971)

(2B-1) J.G. Kirkwood and J. Riseman, J. Chem. Phys., 16, 565 (1948)

(2B-2) K. Raju, Ph.D. dissertation, Department of Chemical Engineering, Michigan State University (1977)

(2B-3) P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York (1953) Ch. 7

(2B-4) P.J. Flory, Ibid., Ch. 14

(2B-5) H.K. Johnston and A. Rudin, Polymer Letters, 9 55 (1971)

(2B-6) A. Einstein, Theory of Brownian Motion, Dover, New York (1956)

(2B-7) R.F. Fedors, AIChE J., 25, 200 (1979)

(2B-8) R.F. Fedors, Ibid., 202

(2B-9) R.F. Fedors, Ibid., 883

(2B-10) R.F. Fedors, Ibid., 716

(2B-11) J.S. Vrentas and J.L. Duda, J. Appl. Polym. Sci., 20, 2569 (1976)

(3A-1) D.B. Bruss and F.H. Stross, J. Polym. Sci., Part A 1, 2439 (1963)

(3A-2) H.G. Elias, Chem. Engr. Techn., 33, 359 (1951)

(3A-3) R.M. Fuoss and D.J. Mead, J. Phys. Chem., 47, 59 (1943)

(3A-4) H.J. Philipp, J. Polym. Sci., 6, 371 (1951)

(3A-5) F.B. Rolfson and H. Coll, Anal. Chem., 36, 888 (1964)

(4A-1) L. Zehnder, Z. Instrumentenk, 11, 275 (1891)

(4A-2) C.S. Caldwell, J.R. Hall and A.L. Babb, Rev. Sci. Instr., 28, 816 (1957)

(4A-3) D.L. Bidlack, Ph.D. Dissertation, Dept. of Chemical Engineering, Michigan State University (1964)

(4D-1) L.J. Gosting and M.S. Morris, J. Am. Chem. Soc., 71 1998 (1949)

(4D-2) D.F. Akeley and J.L. Gosting, J. Am. Chem. Soc., 75, 5685 (1953)

(4D-3) J.M. Creeth, J. Am. Chem. Soc., 77, 6428 (1955)

(4D-4) E.L. Cussler and P.J. Dunlop, J. Phys. Chem., 70, 1880 (1966)

(5A-1) H.G. Elias, Michigan Molecular Institute Manuscript No. 23/E 141, Midland, Michigan (1973)

(5B-1) H.G. Elias and H. Lys, *Makromol. Chem.*, *96*, 64 (1966)

(5B-2) H.G. Elias and R. Bareiss, Chimia, *21*, 53 (1967)

(5B-3) K. Sǒlc and H.G. Elias, *J. Polym. Sci.*, *Polym. Phys. Ed.*., *11*, 137 (1973)

(5B-4) H.G. Elias, *The Study of Association and Aggregation Via Light Scattering*, in *Light Scattering from Polymer Solutions*, Ed. by M.B. Huglin, Academic Press, London (1972)

(5C-1) F. Dolezalek, *Z. Physik. Chem.*, *64*, 727 (1908)

(5C-2) W.G. McMillan and J.E. Mayer, *J. Chem. Phys.*, *13* 276 (1945)

(5C-3) K. Sǒlc and H.G. Elias, *J. Polym. Sci.*, *Polym. Phys. Ed.*, *11*, 137 (1973)

(5C-4) H.G. Elias and R. Bareiss, Chimia, *21*, 53 (1967)

(5C-5) K.H. Meyer and A. van der Wyk, *Helv. Chim. Acta*, *20*, 1321 (1937)

(5C-6) H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row Publishers, New York, 146 (1971)

(5C-7) B.H. Zimm, *J. Chem. Phys.*, *14*, 164 (1946)

(5D-1) H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row Publishers, New York (1971)

(5D-2) C.A. Daniels and E.A. Collins, *J. Macromol. Sci.*, Phys. Ed., *B* *10(2)*, 287 (1974)

(5D-3) N. Yamada, N. Yokouchi, H. Sato and R. Nakamura, *Reports on Progress in Polymer Physics in Japan*, *8* 27 (1965)

(5D-4) A.M. Afifi-Effat and J.N. Hay, *J. Polym. Sci.*, Part B, *9*, 651 (1971)

(5D-5) H.G. Elias and H.P. Lys, *Die Makromol. Chemie*, *80*, 229 (1964)

(5D-6) F.F. Nord, M. Bier and S.N. Timasheft, *J. Am. Chem. Soc.*, *73*, 289 (1951)

(5D-7) J. Gerber and H.G. Elias, *Die Makromol. Chemie*, *112* 142 (1968)

(5D-8) G. Roßkopf, J. Polawka, G. Rehage and W. Borchard, Ber. Bunsenges *Phys. Chem.*, *83*, 360 (1979)

(6A-1) J.O. Hirschfelder, C.F. Curtiss and R.B. Bird., *Molecular Theory of Gases and Liquids*, Wiley, New York (1954)

(6A-2) S.R. deGroot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, Netherlands (1962)

(6A-3) I. Prigogine, *Thermodynamics of Irreversible Processes*, Interscience Publishers, New York (1961)

(6A-4) E.N. Lightfoot and E.L. Cussler, Jr., "Chemical Engineering Progress Symposium Series," No. 58, Vol. *61*, 71 (1965)

(6A-5) L. Onsager, *Phys. Rev.*, *37*, 405 (1931); *38*, 2265 (1931)

(6A-6) G.J. Hooyman and S.R. deGroot, *Physica*, *21*, 73 (1955)

(6B-1) R.F. Fedors, *AIChE J.*, *25*, 883 (1979)

(6B-2) C.C. Han, *Polymer*, *20*, 259 (1979)

(6B-3) H.G. Elias, *Die Makromolekulare Chemis*, *122*, 264 (1969)

(6C-1) R.F. Fedors, *AIChE J.*, *25*, 716 (1979)

(6C-2) D.L. Bidlack, T.K. Kett, C.M. Kelley and D.K. Anderson, *J. Chem. Eng. Data*, *14*, 342 (1969)