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DIFFUSION IN DILUTE POLYTETRAHYDROFURAN SOLUTION

Won Hong Lee*, Joe Lin and Donald K. Anderson

* Dept. of Chemical Engineering, Sogang Univ., Seoul, Korea
Dept. of Chemical Engineering, Michigan State Univ., U.S.A.

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Abstracts — The diffusion coefficients of four polymer-solvent mixtures at 34.0°C were measured using a Mach-Zehnder diffusiometer. Monodisperse ($M_w/M_n < 1.05$) polytetrahydrofuran (PTHF) with and without OH-end group were chosen for this work to study the effects of association of polymer molecules on the diffusion coefficient. In order to minimize the interaction between solvent and polymer molecules, bromobenzene having no hydrogen bond-forming capability was employed as a solvent. The experimental results showed that the OH end group indeed affected diffusion property of dilute polymer solution. An association model was developed in this work and the experimental results were interpreted based on the model.

INTRODUCTION

The concentration dependence of the diffusion coefficient of polymer molecules has been of great interest to scientists and engineers for a long time. As a result of extensive studies, predictive theories are available for diffusion coefficient in dilute polymer solution [1,2,3]. Vrentas and Duda [4] pointed out that diffusion coefficient in dilute polymer solution is governed by at least three factors: thermodynamic, hydrodynamic, and volumetric. These theories provide good agreements for many nonelectrolyte, nonassociating polymer-solvent systems.

However, there exists no satisfactory theory for associating polymer solution. Polymer molecules in solution often associate via secondary binding force (such as hydrogen bonding) to form larger polymer molecules thus changing their properties[5]. Examples are synthetic polymers consisting of proton donating and proton accepting pairs such as polycarboxylic acid-polyethylene oxide and polycarboxylic acid-polyvinyl alcohol. Relatively few studies may be found on associating system. Associating system is more difficult to understand than nonassociating system because the nature of association must also be taken into account. This kind of system may no longer be considered as a binary system but a multicomponent system consisting of polymer unimers, dimers, trimers and so on.

This work aims at investigating the effects of molecular association on diffusion coefficient through measurement of diffusion coefficient of polymer molecules in dilute solution. An expression for the concentration dependence of the diffusion coefficient of associating polymer system is derived by incorperating the effect of molecular association into the osmotic pressure expression which is then related to the chemical potential. The phenomenological theory of molecular diffusion is used to obtain the final expression for the concentration dependence of the diffusion coefficient.

THEORY

Molecular Association

Polymer molecules associate with one another via physical bonds, forming larger molecules. The extent of association is affected by the mechanism of association, the chemical structures of polymer and solvent, solute concentration, temperature, and pressure. Several types of association may be classified[5]. This work focuses on the type of association, usually called open association, in which like molecules associate in the following manner:

$$\begin{aligned} A_1+A_1 &\overset{K_2}{\rightleftharpoons} A_2 \\ A_1+A_2 &\overset{K_3}{\rightleftharpoons} A_3 \\ \vdots \quad \vdots \quad & \quad \vdots \\ A_1+A_{n-1} &\overset{K_n}{\rightleftharpoons} A_n \end{aligned} \tag{1}$$

where A_i represents i-mer and K_i is the association equillibrium constant of the formation of i-mer. For mathematical derivation n is allowed to approach infinity. Assuming the associogenic groups are far apart all K_i's may be replaced by a constant K.

In dilute solution, the polymer molecules mainly

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* To whom all correspondence should be addressed.

consist of unimers, thus this model may be quite reasonable representation of actual association mechanism.

The molecular distribution of an associating polymer solution changes with the polymer concentration ρ_p. For open association, the molecular concentration of i-mer is given by

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

Summing all the C_i's the total molar concentration of the polymer

$$C_p = \sum_{i=1}^{\infty} C_i = \frac{C_1}{1-KC_1} \tag{3}$$

The number average molecular weight

$$M_p = \frac{\rho_p}{C_p} = \frac{M_1}{2}\left[1+\sqrt{1+4\,(K\rho_p/M_1)}\right] \tag{4}$$

Diffusion Coefficient

If the open associating system is treated as a pseudo-binary system, the mutual diffusion coefficient may be related by

$$D = \left(\frac{1-\hat{V}_p\rho_p}{N_A\ f_{sp}}\right)\left(\frac{M_p}{M_s}\right)\cdot\rho_p\left(\frac{\partial\mu_s}{\partial\rho_p}\right)_{T,\,P} \tag{5}$$

Due to the colligative characteristics of osmotic pressure, the observed osmotic pressure for the system can be expressed as

$$\frac{\Pi}{\rho_p RT} = \frac{1}{M_p} + A_2^*\rho_p + \cdots \tag{6}$$

This expression may be applied to open associating polymer solution by substituting eq. (4) for M_p. Note that A_2^* is also a function of the association. A functional form of A_2^* was derived as [6]

$$A_2^* = A_{21}\,(M_1/M_p)^{\alpha} \tag{7}$$

Substituting eqs. (4) and (7) into eq. (6)

$$\frac{\Pi}{\rho_p RT} = \frac{2}{M_1\left[1+\sqrt{1+K\rho_p/M_1}\right]} + A_{21}\left(\frac{M_1}{M_p}\right)^{\alpha}\rho_p + \cdots \tag{8}$$

It should be noted that for K = 0, the above expression is reduced to the nonassociating case. Since $\mu_s = -\Pi\hat{V}_s$, $\left(\frac{\partial\mu_s}{\partial\rho_p}\right)_{T,\,P}$ may be obtained by differentiating eq. (8) with respect to ρ_p. Further if only the two terms of $\hat{V}_p$, $\hat{V}_s$, and f_{sp} in series forms are used:

$$\hat{V}_p = \hat{V}_{po}(1+a_1\rho_p) \tag{9a}$$

$$\hat{V}_s = \hat{V}_{so}(1+b_1\rho_p) \tag{9b}$$

$$f_{sp} = f_{spo}(1+k_s\rho_p) \tag{9c}$$

When these are substituted into eq. (5) the final expression for D for open associating dilute polymer solution is given

$$\begin{aligned}\frac{D}{D_o} = 1 - \Big\{&\frac{1}{M_1}\,\frac{2K}{X(1+X)} - 2A_{21}M_1\left(\frac{2}{1+X}\right)^{\alpha-1} \\ &+ 2\hat{V}_{po}+k_s+b_1\Big\}\rho_p - \Big[\alpha KA_{21}\frac{1}{X}\left(\frac{2}{1+X}\right)^{\alpha} \\ &+ (2\hat{V}_{po}+k_s+b_1)\cdot\Big\{\frac{1}{M_1}\cdot\frac{2K}{X(1+X)} - 2A_{21}M_1 \\ &\left(\frac{2}{1+X}\right)^{\alpha-1}\Big\}\Big]\rho_p^2 + \cdots\end{aligned} \tag{10}$$

where $X = \sqrt{1+4K\rho_p/M_1}$

The initial slope of D/Do vs ρ_p may be obtained

$$\frac{d}{d\rho_p}\left(\frac{D}{D_o}\right)\Big|_{\rho_p=0} = 2A_{21}M_1 - k_s - b_1 - 2\hat{V}_{po} - \frac{K}{M_1} \tag{11}$$

Compared with the nonassociating system, an extra term $-K/M_1$ occurs in the associating system. Depending on the magnitude of K and M_1 the initial slope may take either a positive or negative value. Thus this associating strength term K/M_1 may play an important role in the behavior of open associating system.

EXPERIMENT

The diffusion coefficients of polytetrahydrofuran (PTHF) in bromobenzene (BB) solutions were measured by the use of a Mach-Zehnder interferometer. The temperature of the polymer solutions was controlled at 34° ± 0.1°C. Reagent grade BB (Fisher Scientific Co.) was distilled before use. The PTHF polymer samples designated as A1, A2, B1, and B2 were purchased from Polymer Laboratories LTD. (Church Stretton Strewsbury, U.K.) and their characteristics are listed in Table 1. The polymer samples were used without further purification.

A Mach-Zehnder interferometer described by Caldwell [7] was used to study the diffusion in polymer solution. Two solutions of slightly different concentration are carefully layered, one on top of the other, into an optical diffusion cell and free diffusion allowed to take place after a sharp interface formed between these solutions. The cell is immersed in a constant temperature bath, and the diffusion process in followed by taking pictures of the interference fringe patterns caused by the diffusion process at predetermined time intervals. A

Table 1. Characteristics of PTHF samples.

Polymer Code	$\overline{Mn}$	Polydispersity	End-groups
A 1	281, 000	< 1. 05	$-CH_3$
A 2	30, 000	< 1. 05	$-CH_3$
B 1	7, 660	< 1. 05	$-OH$
B 2	2, 500	< 1. 05	$-OH$

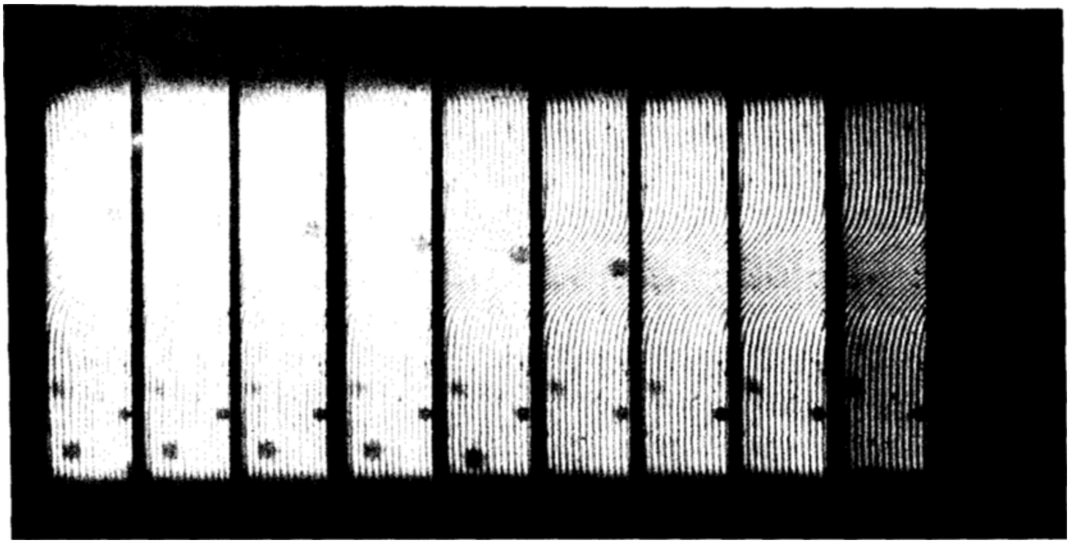

Fig. 1. Typical set of photographs taken during diffusion run.

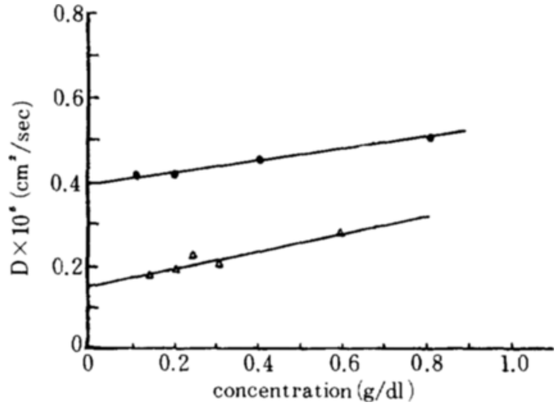

Fig. 2. Concentration dependence of diffusion coefficients of non-associating PTHF - BB solutions at 34.0° C.
PTHF-A 1 in BB···△, PTHF-A 2 in BB···●.

typical series of exposures taken for one run is shown in Fig. 1. The details involved in the experimental procedures and the method for obtaining diffusion coefficient from the interference fringe pattern are found elsewhere [8]. The diffusion coefficient obtained in this way is assumed to be that of a concentration which is the average of the two solution concentrations.

RESULTS AND DISCUSSIONS

The concentration dependence of the diffusion coefficients for the various PTHF-solvent system is given in Fig. 2 and 3 along with theoretical curves.. From the results shown in Fig. 2, it is evident that the concentration dependence of the diffusion coefficient for the systems with CH_3end group, can be approximated by a linear relationship over the entire concentration range investigated. These results agree with the prediction of the theory for nonassociation polymer systems.

Althought the interferometric method will not provide data at low concentration in all cases, the results for the systems with OH end group given in Fig. 3 clearly indicate increased diffusion coefficients at low concentrations. 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. These results are in agreement with the prediction of the association model developed in this work. The theoretical curves were determined based on eq. (10). Two parameter theory [9] and Kirkwood and Riseman [10] theory were used to calculate values for all the parameters except K which was estimated by fitting the equation to the diffusion data. For these calculations we have set the Mark-Houwink parameters k and a to be 0.131 ml/g and 0.6 respectively, $b_1 = 0$, $\hat{V}_{po} = 1.114$ cm^3/g and $r_o/M_1^{1/2} = 8.6 \times 20^{-2}$nm.
The values for K and D_0 are listed in Table 2.
As mentioned before the initial slope of the D/D_0 vs ρ_p curve can be negative depending on the magnitude of K and M_1.

The theoretical prediction shows that the diffusion coefficient increases sharply with decreasing polymer concentration in dilute associating polymer solutions. There exists a very narrow range of effective association strength K/M_1 within which the association of polymer molecules is detectable. For low K/M_1 the association ef-

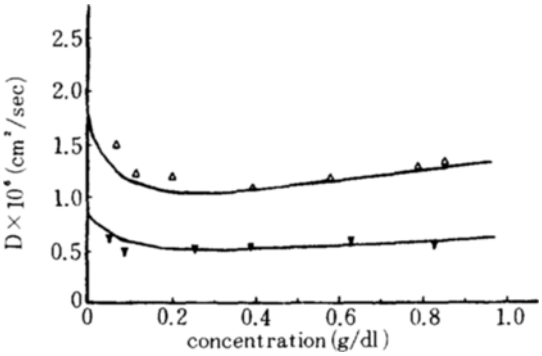

Fig. 3. Concentration dependence of diffusion coefficients of associating PTHF-BB solutions at 34.0°C.

PTHF-B 1 in BB…▼, PTHF-B 2 in BB…△. (The curves were determined based on eq. (10))

Table 2. Summary of diffusion coefficient data for PTHF-BB systems at 34.0°C.

Polymer-Solvent	$K/Mn \times 10^{-4}$ (cc/gm)	$D_0 \times 10^6$ (cm²/sec)
A 1 - BB	---	0. 1516
A 2 - BB	---	0. 3936
B 1 - BB	0. 065	0. 8009
B 2 - BB	0. 200	1. 8250

fect would be insignificant compared to other interaction. On the other hand, if K/M_1 is high, the association effect would be complete at such low concentrations that accurate diffusion measurements are not possible. The effect of association on diffusion rate becomes much less significant at higher concentration than it is in the infinitely dilute region.

The finding that the diffusion coefficient increases sharply with decreasing polymer concentration in dilute 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. Unfortunately accurate measurements of diffusion coefficient in the infinitely dilute region is difficult (or impossible in some cases) by using traditional apparatus. The association phenomena might therefore be overlooked. It is interesting to point out that the limiting diffusion coefficients of associating systems 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 also explain the lack of agreement between D_0 values observed in some laboratories and those predicted by theoretical considerations [11, 12].

CONCLUSIONS

An association model is presented which provide an explanation for some conflicts between experimental observation and existing thermodynamics and diffusion theories of nonassociating 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 intermolecular interaction. This prediction is consistent with the experimental observations.

ACKNOWLEDGEMENT

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NOMENCLATURE

a : Mark-Houwink parameter
a_1 : coefficient in series given by eq. (9a)
A_{21} : second virial coefficient of unimer
A_2^* : second virial coefficient defined by eq. (6)
b_1 : coefficient in series given by eq. (9b)
C_i : molar concentration of i-mer
C_p : molar concentration of polymer defined by eq. (4)
D : mutual diffusion coefficient polymer
D_0 : mutual diffusion coefficient at zero polymer concentration
f_{sp} : friction coefficient of polymer molecule difined by eq. (9c)
f_{spo} : friction coefficient at zero polymer concentration
K_i : association constant of the formation of i-mer
K : association constant
k : Mark-Houwink parameter
k_s : coefficient in series given by eq. (9c)
M_1 : molecular weight of unimer
M_p : number average molecular weight defined by eq.(4)
M_s : molecular weight of solvent molecule
N_A : Avogadro's number
p : pressure
R : gas constant per mole
r_0 : end to end distance of unperturbed chain
T : temperatue
$\bar{V}_s$: partial molar volume of solvent
$\hat{V}_p$: partial specificvolume of polymer
$\hat{V}_s$: partial specific volume of solvent
$\hat{V}_{p0}$: partial specific volume at zero polymer concentration
$\hat{V}_{s0}$: partial specific volume of solvent at zero polymer concentration

Π : osmotic pressure
α : parameter defined by eq. (7)
μ_s : chemical potential of solvent per mole
ρ_p : polymer cocentration

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