ΔG	= partial molar Gibbs' free energy change of mixing	[cal/mol]
ΔH	= partial molar enthalpy change of mixing	[cal/mol]
ΔH_{vap}	= latent heat of vaporization	[cal/mol]
M	= molecular weight	
N_{seg}	= number of segments in a polymer molecule	[-]
N_{Si}	= number of silicon atoms in a molecule	[-]
n	= molar number	[mol]
R	= gas constant	[cal/mol·°K]
ΔS	= partial molar entropy change of mixing	[cal/mol·°K]
T	= temperature	[°K]
V	= molar volume	[cm ³ /mol]
X	= mole fraction	[-]
<Greek>		
δ	= solubility parameter	[cal ^{1/2} /cm ^{3/2}]
ϵ	= cohesive energy density	[cal/cm ³]
ν	= kinetic viscosity	[cm ² /sec]
ϕ	= volume fraction	[-]
χ	= Flory interaction parameter	[-]
<Subscript>		
H	= enthalpy	
i	= i -th constitutive group	
M	= mixing	
p	= polymer	
S	= entropy	
seg	= segment	

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DIFFUSION OF NON-POLYMERIC AND POLYMERIC MOLECULE IN CHAIN POLYMER LIQUID — A THEORETICAL EXPLANATION OF ANOMALOUS BEHAVIOR OF DIFFUSIVITY IN POLYMERIC SYSTEM* —

HISAHIKO WATANABE AND TERUKATSU MIYAUCHI
Department of Chemical Engineering, University of Tokyo,
Tokyo, Japan

This work is concerned with the diffusivity in polymeric two-component systems in which the penetrant concentration is infinitely dilute. In polymeric systems the Wilke-Chang equation does not hold, and diffusivity shows an anomalous behavior; that is, it shows a constant value regardless of medium molecular weight. This anomaly is accounted for in this work.

The diffusivity of non-polymeric and polymeric molecules through a polymeric medium has been derived theoretically as an extension of the free-volume theory by Bueche. With this formulation, a simple expression has been developed to correlate diffusivity, viscosity, temperature and molecular weight of the system. Good agreement with the experimental data for the polydimethylsiloxane system is obtained. It is found that $D\eta/T$ is proportional to $M^{3.5}$ for the range of $M > M_b$, and to M for the range of $M < M_b$, where M is the molecular weight of polymeric medium and M_b is a characteristic value.

1. Introduction

There have been a great number of theoretical as

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〒113 東京都文京区本郷7-3-1

東京大学工学部化学工学科 渡辺尚彦

Fig. 1 The diffusivity of iodine in various solvents vs. solvent viscosity³⁵⁾

Fig. 2 The diffusivity of benzene and PDS in PDS matrix.³³⁾ M_{p2} is the molecular weight of medium PDS.

well as experimental investigations of diffusivity in non-polymeric liquid phase. For one-component self-diffusivity, the theory of absolute processes by Eyring and his co-workers^{10,13)} its modifications^{20,22,26)} and others^{4,8,17,27)} have been presented. Among these, Eyring's equation is the simplest in form:

$$\frac{D\eta}{T} = \frac{k}{6} \left(\frac{N_A}{V} \right)^{1/3} \quad (1)$$

For two-component systems, however, theoretical treatments^{12,15,18,23)} have some difficulties in practical use. Therefore, empirical correlations, such as Wilke and Chang's equation^{36,37)}, its modifications^{11,25,29,32)} and others^{16,19,21,24,31)} are commonly used. The Wilke-Chang equation is as follows:

$$\frac{D_{12}\eta_2}{T} = 7.4 \times 10^{-10} \frac{(bM_2)^{1/2}}{V_1^{0.6}} \quad (2)$$

* PDS is a linear chain polymer consisting of siloxane units.
 $(\text{CH}_3)_3\text{Si}-(\text{OSi}(\text{CH}_3)_2)_n-\text{CH}_3$

When the size of penetrant molecule is sufficiently large compared with that of medium liquid, the Stokes-Einstein equation⁹⁾ can be applied:

$$\frac{D_{12}\eta_2}{T} = \frac{k}{6\pi r_1} \quad (3)$$

By the use of the results of these investigations above, diffusivities of one- and two-component non-polymeric systems are predictable within about 50 per cent error.

On the contrary, anomalous behavior of diffusivity has been reported for viscous liquid^{19,21)}, in particular for highly polymeric medium^{33,35)}. Most of all, the experimental systems used for Wilke-Chang's correlation are less viscous than a few centipoise^{36,37)}. For more viscous systems, Wilke-Chang's equation gives fairly smaller values than those of experiment^{14,19)}.

This tendency turns out to be decisive when the diffusion medium is composed of chain polymer molecules^{33,35)}. The diffusivities D_{12} of iodine (1) in various kinds of liquid medium (2), available in the literature, are plotted against the medium viscosity η_2 in Fig. 1³⁵⁾. $\ln(D_{12}/T)$ vs. $\ln\eta_2$ plot for each non-polymeric homologue liquid shows parallel straight line, with a gradient of -0.7 . (This implies the relation $\eta \propto M^{1.2}$ in Wilke-Chang's correlation.) However, the diffusivity of iodine in polydimethylsiloxane* (PDS) behaves in an entirely different manner, approaching a constant regardless of medium molecular weight, when the polymer chain length grows sufficiently high³⁵⁾. The diffusivity of benzene in PDS is also reported³³⁾ to show similar behavior (Fig. 2). Tanner³³⁾ measured the diffusivity of PDS in PDS, varying molecular weight of penetrant and medium component and also obtained a constant diffusivity region (see Fig. 2). These have common characteristics: (i) When the medium molecular weight M_{p2} does not reach a critical value, diffusivity D_{12} depends on medium molecular weight M_{p2} , but is considerably insensitive compared with that in non-polymeric system. (ii) When M_{p2} exceeds a certain critical molecular weight, the diffusivity remains constant regardless of molecular weight M_{p2} .

This anomalous behavior of diffusivity in polymeric systems cannot be interpreted by the use of theoretical nor empirical equations for non-polymeric systems. This originates in the constitutional difference between polymeric and non-polymeric systems.

A number of investigations have been presented^{1,6)} on physical properties of polymer. However, most quantitative treatments of diffusivity contain some physical quantities which are not available in common. As an exception, a simple relationship correlating diffusivity, viscosity, temperature and molar volume was given by Bueche¹⁾ for one-component self-diffusivity (see section 2.3). This work extends that of Bueche to two-component systems in which penetrant molecule is very dilute. In the next section, the treatment of chain polymer by a hole model is described. Then, in section 3, two-component diffusivity equations in polymeric systems are derived by the use of

free-volume theory. A fairly complete explanation of the anomalous behavior as pointed out above is given in section 4, using the equations derived in section 3.

2. Description of the Behavior of Chain Polymer by Hole Model

2.1 Diffusivity of small molecule and chain polymer molecule

Let us consider a simple liquid composed of small molecules. The diffusivity of a molecule is given as follows¹⁾:

$$D = \phi \delta^2 / 6 \quad (4)$$

where ϕ is the mean jump frequency and δ is the mean jump distance of the molecule. Eq.(4) holds good not only for one-component system but also for two-component system, as long as the system is infinitely dilute. This is because when the system is sufficiently dilute, the diffusion medium can be regarded as homogeneous. Consequently, a mean jump distance δ and a mean jump frequency ϕ of penetrant molecule can be uniquely defined.

The method used to derive diffusivity in non-polymeric liquid described above can be extended to chain polymer systems with ease¹⁾. Let us suppose that a chain polymer molecule consists of N segmental units; each segment is a in length and is composed of several repeating molecular units. When we suppose, further, that these segments are completely freely oriented and make jumps independently in each other, the self-diffusivity D_{pp} of one-component polymer liquid is obtained¹⁾ as follows, substituting the jump frequency $N\phi_s$ and jump distance δ_s/N of a polymer molecule to Eq.(4):

$$D_{pp} = \phi_s \delta_s^2 / 6N \quad (5)$$

where ϕ_s and δ_s are jump frequency and jump distance of segmental units, respectively.

2.2 The effect of entanglement

In the previous section, the motion of each polymer molecule is assumed independent of each other without any entanglement. However, we must consider the effect of entanglement when molecular weight of polymer grows sufficiently high. In general, Eq.(5) is also applicable to entangled chain polymer systems¹⁾, provided N is replaced by a modified value N^* , which is larger than N .

$$D_{p,p} = \phi_s \delta_s^2 / 6N^* \quad (6)$$

According to Bueche^{1,3)} N^* is approximated as follows

$$(a) \quad M_p < 2M_e: \quad N^* f_{os} = N f_{os} \quad (7a)$$

$$(b) \quad M_p > 2M_e: \quad N^* f_{os} = N f_{os} (\rho N_A / 48) (M / M_e)^2 M^{1/2} (a^2 / M_{seg})^{3/2}$$

$$\times \sum_{n=1}^{\infty} \sigma^n (2n-1)^{3/2} \quad (7b)$$

where f_{os} is the friction factor of a segmental unit, and is related to diffusivity by

$$D_{p,p} = kT / N^* f_{os} \quad (8)$$

σ is slippage factor. M and M_{seg} are, respectively, the molecular weight of polymer molecule and that of

segmental unit. M_e is a kind of critical molecular weight, corresponding to several segmental units between entangling points. The comparison of Eqs.(6) and (8) gives

$$f_{os} = 6kT / \phi_s \delta_s^2 \quad (9)$$

2.3 A simple relation between diffusivity and viscosity (one-component polymeric system)

The viscosity of polymer solution and polymer melt is given as follows^{1,7)}:

$$\eta_p = (\rho N_A / 36) (a^2 / M_{seg}) N^* f_{os} \quad (10)$$

When we combine the equation of diffusivity Eq.(8) and that of viscosity Eq.(10) for polymeric system, a simple equation is obtained as follows¹⁾:

$$\frac{D_{p,p} \eta_p}{T} = \left(\frac{k \rho N_A}{36} \right) \left(\frac{a^2}{M_{seg}} \right) = \frac{k}{36} \left(\frac{N_A}{V_{seg}} \right)^{1/3} \quad (11)$$

Eq.(11) is similar to Eq.(1) for non-polymeric liquid. It should be noticed, however, that the right-hand side is not a function of molar volume of the whole polymer molecule but that of a segmental unit. Eq.(11) says that $D_{p,p} \eta_p / T$ will be constant for a homologue polymeric series.

The relation $D_{p,p} \eta_p / T = \text{constant}$, is experimentally observed¹⁾ in both condensed polymeric solution and polymer melt of poly-*n*-butyl acrylate, polystyrene and polymethylene.

3. Two-component Diffusivity in Chain Polymer Liquids

3.1 The expression of mean jump frequency by free-volume theory

The simple equation relating the diffusivity and viscosity of polymeric system described in the previous section is confirmed to one-component system. The objective of this work is to extend this kind of equation to two-component systems. Diffusivity is generally given by Eq.(4). It is unlikely that the distance δ which a molecule travels in jumping from one equilibrium position to another can vary too greatly from material to material. Therefore the variation of diffusivity from system to system, often many orders of magnitude, is mainly the result of the different value of jump frequencies¹⁾ ϕ .

According to the free volume theory of Bueche^{1,2)} and Cohen and Turnbull⁵⁾, jump frequency ϕ of a small molecule or a segment is considered to be proportional to the probability that the molecule or the segment is adjacent to a hole which is larger than a certain critical volume v^* . Since this probability is proportional to $\exp(-\beta^* v^* / v_f)$ over a glass-transition temperature, jump frequency ϕ is given in the end as follows by the free-volume theory¹⁾:

$$\phi = \phi_o \exp(-\beta^* v^* / v_f) \quad (12)$$

where

$$\beta^* = \ln(v^* / v_f) - 1 \quad (13)$$

v_f is a mean free volume per a molecule or a segment (V_f / N_A) and β^* is considered to be a constant value near 1¹⁾.

3. 2 Diffusivity in polymeric medium—Case I: diffusivity of a small molecule—

This section concerns the diffusivity of a small molecule, the size of which is about equal to that of a segmental unit of the medium polymer molecules. The expression of jump frequency ϕ given above is that for one-component system. For the treatment of two-component diffusion processes, however, the individual role of penetrant and medium molecule should be appropriately distinguished. In Eq.(12), the critical free volume v^* must be a quantity concerned with penetrant molecule (1), while the mean free volume v_f is concerned with medium molecule ($p2$). The probability constant ϕ_0 may be interpreted as a limit of ϕ when v_f approaches infinity. Therefore, ϕ_0 may be concerned with penetrant molecule (1). Based on these considerations, the diffusivity $D_{1,p2}$ and jump frequency $\phi_{1,p2}$ of molecule (1) in chain polymer medium ($p2$) may be expressed as follows:

$$D_{1,p2} = \phi_{1,p2} \delta_s^2 / 6 \quad (14)$$

$$\phi_{1,p2} = \phi_{01} \exp(-\beta^* v_1^* / v_{fs}) \quad (15)$$

On the other hand, the jump frequency of segmental unit of polymer is given by Eq.(12):

$$\phi_s = \phi_{0s} \exp(-\beta^* v_s^* / v_{fs}) \quad (16)$$

Now, let us take the ratio of diffusivities $D_{1,p2}$ and $D_{p2,p2}$ to cancel unknown parameters, rearranging it by the use of Eqs.(15) and (16):

$$\begin{aligned} \frac{D_{1,p2}}{D_{p2,p2}} &= \frac{\phi_{1,p2} \delta_s^2 / 6}{\phi_s \delta_s^2 / 6 N^*} = \frac{\phi_{1,p2}}{\phi_s} N^* \\ &= \frac{\phi_{01}}{\phi_{0s}} N^* \exp\{-\beta^* (v_1^* - v_s^*) / v_{fs}\} \quad (17) \end{aligned}$$

When the size of penetrant molecule is approximately equal to that of a segmental unit of the polymer medium, we can substitute $v_1^* \approx v_s^*$ and further $\phi_{01} \approx \phi_{0s}$ to Eq.(17) to obtain

$$\frac{D_{1,p2}}{D_{p2,p2}} \approx N^* \quad (18)$$

Eliminating $D_{p2,p2}$ by the use of Eq.(11), we can obtain a simple equation relating diffusivity $D_{1,p2}$ and medium viscosity η_{p2} :

$$\frac{D_{1,p2} \eta_{p2}}{T} \approx \frac{k N^*}{36} \left(\frac{N_A}{V_{seg}} \right)^{1/3} \quad (19)$$

Consequently, the diffusivity $D_{1,p2}$ of a small molecule (1), the size of which is nearly equal to that of a segmental unit of medium, through homologue series of chain polymer liquid medium ($p2$), is given as follows, according to the classification for entanglement effect given by Eq.(7):

(a) When $M_{p2} < 2M_e$: N^* is given by $N^* = N = M_p / M_{seg}$;

The result of substitution to Eq.(19) reduces to

$$\frac{D_{1,p2} \eta_{p2}}{T} \propto M_{p2} \quad (20a)$$

(b) When $M_{p2} > 2M_e$; N^* is proportional to $M_p^{3.5}$, substituting $N = M_p / M_{seg}$ in Eq.(7b).

The result of substitution to Eq.(19) reduces to

$$\frac{D_{1,p2} \eta_{p2}}{T} \propto M_{p2}^{3.5} \quad (20b)$$

3. 3 Diffusivity in polymeric medium—Case II: diffusivity of a chain polymer molecule—

In this section, we deal with the case where the diffusing molecule is not a small molecule but a homologue polymeric one, consisting of N_{p1} segmental units, while the polymeric medium has N_{p2} segmental units in a molecule. Let us repeat that Eq.(5) is derived by considering the jump frequency and jump distance of the center of mass of penetrant polymer molecule. Therefore, N in Eq.(5) and N^* in Eq.(6) are quantities concerned with penetrant polymer molecule. Consequently, the diffusivity $D_{p1,p2}$ is given as follows:

$$D_{p1,p2} = \phi_s \delta_s^2 / 6 N_{p1}^* \quad (21)$$

Although Eq.(21) is good for non-entangling region, it may not be strictly correct to apply Eq.(7) as the entanglement effect N_{p1}^* to two-component diffusivity $D_{p1,p2}$ (Eq.(21)), since the molecular weight of penetrant is different from that of medium molecule. However, as a first approximation, let us use Eq.(7) as the entangling effect for two-component system, too. On the other hand, one-component self-diffusivity $D_{p2,p2}$ is given as follows:

$$D_{p2,p2} = \phi_s \delta_s^2 / 6 N_{p2}^* \quad (22)$$

The ratio of these two diffusivities reduces to

$$\frac{D_{p1,p2}}{D_{p2,p2}} = \frac{N_{p2}^*}{N_{p1}^*} \quad (23)$$

Eliminating $D_{p2,p2}$ by the use of Eq.(11), we obtain

$$\frac{D_{p1,p2} \eta_{p2}}{T} = \frac{k}{36} \left(\frac{N_A}{V_{seg}} \right)^{1/3} \frac{N_{p2}^*}{N_{p1}^*} \quad (24)$$

where N_{p1}^* and N_{p2}^* are given by Eq.(7). According to the molecular weight classification for entanglement effect, Eq.(24) is rewritten as follows:

(a) $M_{p1} < 2M_e$ and $M_{p2} < 2M_e$:

$$\frac{D_{p1,p2} \eta_{p2}}{T} \propto \frac{M_{p2}}{M_{p1}} \quad (25a)$$

(b) $M_{p1} < 2M_e$ and $M_{p2} > 2M_e$:

$$\frac{D_{p1,p2} \eta_{p2}}{T} \propto \frac{M_{p2}^{3.5}}{M_{p1}} \quad (25b)$$

(c) $M_{p1} > 2M_e$ and $M_{p2} < 2M_e$:

$$\frac{D_{p1,p2} \eta_{p2}}{T} \propto \frac{M_{p2}}{M_{p1}} \quad (25c)$$

(d) $M_{p1} > 2M_e$ and $M_{p2} > 2M_e$:

$$\frac{D_{p1,p2} \eta_{p2}}{T} \propto \frac{M_{p2}^{3.5}}{M_{p1}^{3.5}} \quad (25d)$$

where in case (c), the entangling effect of penetrant molecule is neglected because of sufficiently dilute concentration. In case (d), entanglement effect is considered, since the dilute penetrant molecule ($p1$) may be sure to entangle with medium molecules ($p2$); however, if $M_{p1} \gg M_{p2}$, the effect of entanglement will be considerably decreased to give lower power order with M_{p1} ; and if $M_{p1} \ll M_{p2}$, to give higher power order.

4. Discussion: Comparison with Experimental Data

In this section, the theoretical equations derived in

Fig. 3 Plot of diffusivity in PDS homologue liquids as $\ln D_{p2}/T$ vs. $\ln M_{p2}$. M_{p2} is the molecular weight of medium PDS. Encircled points are one-component self-diffusivities.

the previous section are compared with experimental data. And the anomalous behavior in polymeric systems as pointed out in section 1 is theoretically explained.

4.1 A plot of literature data for comparison

There are only a few data available in the literature for our discussion. The diffusivity data of iodine³⁵⁾, benzene³³⁾ and polydimethylsiloxane³³⁾ (PDS) in medium PDS are plotted $\ln(D_{1,p2}\eta_{p2}/T)$ vs. $\ln M_{p2}$ or $\ln(D_{p1,p2}\eta_{p2}/T)$ vs. $\ln M_{p2}$ in Fig. 3, to be compared with theoretically derived equations above. The constant temperature at which diffusivity was measured is 33 °C for both benzene-PDS and PDS-PDS systems³⁴⁾, and is 25 °C for iodine-PDS system³⁵⁾. The viscosity data of PDS are found in manuals³⁰⁾.

Each D_{p2}/T vs. M_{p2} curve is divided into three regions by two border lines; namely a straight line AA' ($M_{p2}=37,000$), which is the critical value $2M_e$ of PDS (see section 4.3), and a curve BB'B'' which represents one-component self-diffusivity. The features of each

region are summarized as follows:

In the right-hand region of the straight line AA', D_{p2}/T is proportional to $M_{p2}^{3.5}$. In the wedge-shaped region intercepted by the straight line AA' and the curve BB'B'', D_{p2}/T is nearly proportional to M_{p2} . In the left-hand region of the curve BB'B'', D_{p2}/T reduces to a constant regardless of M_{p2} , provided M_{p1} is less than $2M_e$. On the other hand, when M_{p1} exceeds the critical molecular weight $2M_e$, the wedge-shaped region disappears and D_{p2}/T is no longer constant, but is proportional to $M_{p2}^{1/3}$ in the left-hand region of the straight line AA'.

For the case of the diffusivity of iodine and benzene in PDS, Fig. 3 shows the proportionality of D_{p2}/T to M_{p2} in the wedge-shaped region and shows a transitional behavior to 3.5 power region at $M_{p2}=40,000$.

4.2 Comparison with the theory

The three regions pointed out above completely agree with theoretical results given in the previous sections. The straight line AA' corresponds to the critical molecular weight $2M_e$ of entanglement effect. In the region where M_{p2} is larger than $2M_e$, D_{p2}/T is proportional to $M_{p2}^{3.5}$, as shown by Eqs.(20b), (25b) and (25d). On the other hand, the curve BB'B'' corresponds to the one-component self-diffusivity equation, Eq.(1) and Eq.(11). In the non-polymeric range, D_{p2}/T decreases in proportion to $V^{-1/3}$, namely to $M^{-1/3}$, since the density of PDS is nearly constant (0.9–1.0 g/cm³) regardless of degree of polymerization. In the polymeric range where medium polymer has enough molecular weight to reach a constant segment size, D_{p2}/T reduces to a constant regardless of M_{p2} .

In the wedge-shaped region between the curve BB'B'' and the straight line AA', the proportionality between D_{p2}/T and M_{p2} corresponds to Eqs.(20a) and (25a). In the left-hand region of the curve BB'B'', D_{p2}/T becomes constant regardless of M_{p2} (or M_2). This is the characteristic feature of the Stokes-Einstein equation (Eq.(3)).

On the contrary, when M_1 exceeds $2M_e$, the wedge-shaped region disappears and the Stokes-Einstein equation is no longer satisfied for two cases: $M_1=40,000$ and $M_1=115,000$ in Fig. 3. This region corresponds to the case (c) in section 3.3, and Eq.(25c) should be satisfied, when the theory derived in this work holds good in this region. Eq.(25c) says that D_{p2}/T is proportional to M_{p2} . Therefore, the behavior of experimental data, namely $D_{p2}/T \propto M_{p2}^{1/2}$, can be regarded as intermediate between the Stokes-Einstein equation and Eq.(25c). There is no detailed explanation for this discrepancy yet. However, some qualitative explanations such as what follows are possible:

The penetrant high polymer molecules may diffuse through small molecular medium, forming coils with its long chain segments. The entanglement effect of penetrant polymer may happen to fasten the coils to decrease its effective frictional force in diffusion process. Then the diffusivity may be increased, and D_{p2}/T might deviate from Eq.(25c). On the other hand,

penetrant polymers cannot form coils when medium molecules are not small; therefore, Eq.(25d) holds good.

The concentration of penetrant molecules is 10 per cent weight fraction in benzene-PDS and PDS-PDS systems³³. Although this does not seem to be dilute enough to satisfy the no-interaction assumption concerning penetrant molecules, good agreement between theory and experiment is obtained. The concentration of penetrant in iodine-PDS system is less than 1 per cent (weight)³⁵.

4. 3 The explanation of constant diffusivity

The remarkable feature of constant diffusivity in polymeric system corresponds to $D\eta/T \propto M_{p2}^{3.5}$ in our equation. The viscosity of condensed polymer solution and polymer melt is known¹ to be proportional to $M^{3.5}$ without exception in the range of higher molecular weight over a critical value M_b .

$$\eta \propto M^{3.5} \quad (M > M_b) \quad (26)$$

This critical molecular weight M_b is approximately equal to $2M_e$ ¹. Substituting Eq.(26) to Eqs.(20b), (25b) and (25d), the diffusivity $D_{1,p2}$ or $D_{p1,p2}$ for the range of sufficiently large molecular weight medium reduces to:

$$\begin{aligned} D_{1,p2}(\text{or } D_{p1,p2}) &= (\text{constant}) \frac{M_{p2}^{3.5}}{\eta_{p2}} \cdot T \\ &= (\text{constant})' T \end{aligned} \quad (27)$$

Eq.(27) indicates a constant diffusivity at constant temperature regardless of medium molecular weight M_{p2} . Therefore, the critical molecular weight for constant diffusivity may be equal to $2M_e$ or M_b , which is 37,000 for PDS¹. However, when M_{p1} exceeds $2M_e$ or M_b , the critical value for constant diffusivity seems to be M_{p1} itself as shown in Fig. 2.

4. 4 The ideal characteristic of PDS

As is shown in the previous sections, the experimental result in PDS system considerably well satisfies the theoretical equations derived in this work. This good agreement may be attributed to the distinguished characteristics of PDS as a long-chain polymer molecule. That is, the segmental motion of PDS molecule is nearly completely freely oriented. This is supported by the fact that the activation energy for viscous flow of PDS is known to be peculiarly low compared with other substances, e.g. *n*-paraffins²⁸. Furthermore, this free motion of segments of PDS was confirmed by measurement of dipole moment and electron diffraction²⁸. Moreover, PDS is considered to have low glass transition temperature T_g ; T_g of silicon rubber is -123°C ¹. Therefore, room temperature is sufficiently high over T_g for PDS system. Consequently, PDS system may be regarded as an ideal system for the theory based on completely freely oriented segmental motion. For other polymeric systems in which segmental motion is considerably constrained, this theory may be applied with some modifications. However, there is not enough necessary basic data available for general formulation yet.

5. Conclusion

- (1) Two-component diffusivity for chain polymer system is derived theoretically as an extension of the free-volume theory of Bueche. With this equation, diffusivity, viscosity, temperature and molecular weight are correlated in a simple form.
- (2) The behavior of diffusivity of non-polymeric and polymeric molecules in a polymeric medium is found to be classified into three regions by consideration of the entanglement effect.
- (3) These theoretical equations are shown to be in good agreement with the experimental results in PDS systems, in which an anomalous behavior of diffusivity has been pointed out. The anomaly is explained in this work.

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Nomenclature

a	= length of a segmental unit	[cm]
b	= association parameter	
D	= diffusivity	[cm ² /sec]
$D_{1,2}$	= diffusivity of component 1 through medium component 2	[cm ² /sec]
f_0	= molecular friction factor	[g/sec]
f_{os}	= segmental friction factor	[g/sec]
k	= Boltzmann constant	[erg/deg]
M	= molecular weight	[g/mol]
M_{seg}	= molecular weight corresponding to segmental unit	[g/mol]
M_e	= molecular weight corresponding to several segmental units between entangling sites	[g/mol]
N_A	= Avogadro number	[1/mol]
N	= number of segmental units in a molecule	[—]
N^*	= modified number of segmental units in a molecule	[—]
r	= radius of molecule	[cm]
T	= temperature	[°K]
t	= time	[sec]
V	= molar volume	[cm ³ /mol]
V_f	= molar free volume	[cm ³ /mol]
V_{seg}	= molar volume per segmental unit	[cm ³ /mol]
v_f	= free volume per molecule or segmental unit	[cm ³]
v^*	= critical free volume	[cm ³]
<Greck>		
β^*	= defined by Eq.(13)	[—]
δ	= mean jump distance	[cc]
η	= viscosity	[g/cm·sec]
ρ	= density	[g/cm ³]
σ	= slippage factor	[—]
ϕ	= mean jump frequency	[1/sec]
ϕ_0	= proportionality constant	[1/sec]
<Subscript>		
p	= polymer	
s	= segment	
1,2	= component 1 and 2; component 1 for penetrant molecule; component 2 for medium molecule	

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APPLICATION OF THE VAN DER WAALS ONE FLUID THEORY TO PREDICT VAPOR-LIQUID EQUILIBRIA*

EIJI SARASHINA, YASUHIKO ARAI AND
SHOZABURO SAITO

Department of Chemical Engineering, Tohoku University,
Sendai, Japan

The van der Waals one-fluid theory was applied to mixtures of simple molecules and to systems containing carbon dioxide.

The excess properties of mixtures of simple molecules, G^E , H^E and V^E , were well correlated by introducing correction factors, ξ_{12} and η_{12} , for the Lorentz-Berthelot rules for the potential parameters between unlike molecules. Further, these parameters were useful in correlating the vapor-liquid equilibria for mixtures of simple molecules.

Among systems containing carbon dioxide, the vapor-liquid equilibria for carbon dioxide-light hydrocarbon systems and carbon dioxide-fluorocarbon systems were also well correlated by introducing the correction factor, ξ_{12} . On the other hand, systems consisting of carbon dioxide and simple molecules could be successfully correlated by adjusting the critical temperature of the light component.

Introduction

The applicability of the corresponding-states principle to mixtures has been studied by several workers. In applying this principle to mixtures, they usually define the pseudopotential parameters for mixtures

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〒980 仙台市花巻字青葉

東北大学工学部化学工学科 齊藤正三郎