DETERMINATION OF SOLUBILITY PARAMETER FOR SILOXANE SEGMENT — THE SOLUBILITY OF IODINE IN LIQUID POLYDIMETHYLSILOXANE* —

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

The solubility of iodine in PDS (polydimethylsiloxane) has been measured for varying degrees of polymerization (number of silicon atoms) from 2 to 470. The data obtained show good agreement with a solubility equation derived on the basis of the following two assumptions: (1) a PDS molecule is composed of several completely freely oriented segments, and (2) the mixture of these segments and iodine can be treated as a regular solution as far as enthalpy calculation is concerned.

A constant segment solubility parameter δ_s , which is about $7.5 \text{ cal}^{1/2}/\text{cm}^{3/2}$, is obtained regardless of degree of polymerization by the use of this solubility equation. This value is nearly the same as that of silicon rubber from swelling data. On the basis of the discussions above, it is concluded that the size of a segment is nearly equal to that of a siloxane unit. The molecular-attraction constant for a siloxane unit is found to be $580\text{--}600 \text{ cal}^{1/2} \cdot \text{cm}^{3/2}/\text{mol}$.

1. Introduction

This work is concerned with the solubility of low molecular weight species in polydimethylsiloxane. The knowledge of solubility of gases and liquids is important in membrane separation, bonding, dyeing and printing engineering as well as in film and fiber manufacture.

The solubility behavior of solid polymer is considerably more complicated than that of the usual liquid (non-polymeric liquid). When a polymer is dipped in a solvent, the solvent molecules penetrate into the solid polymer structure and swelling of the polymer takes place. When the solvent action is high, the polymer and solvent are mixed with each other at any ratio (infinite swelling)⁴⁾. In this respect, polymer behaves in a liquid-like manner. In fact, the solubility of an amorphous polymer can be treated in the same way as that of a nonpolymeric liquid. On the other hand, polymers with crosslinked structure swell only to the extent that the contracting force of polymer molecule is balanced with the diffusive force of solvent.

A completely satisfactory statistical mechanical

description of polymer solution is not yet available. However, several approximate semiempirical techniques based on the Flory-Huggins treatment have been presented.^{1,2,3,7,9)}

This work is intended to approach the behavior of solid polymer segments by use of the knowledge of liquid polymer segments, which have much simpler structures than those of solid polymer. In what follows, solubility of iodine in liquid polydimethylsiloxane $\text{Me}_3\text{Si}(\text{-OSiMe}_2\text{-})_{m-1}\text{Me}$ is presented, and the solubility parameter for liquid polydimethylsiloxane is determined on the basis of the assumption that the polymer molecule consists of completely freely oriented segmental chain units. The solubility parameter thus obtained is used for solubility equation for liquid polymer, which describes the solubility dependence upon degrees of polymerization.

2. Experimental

2.1 Procedure and material

About 50 ml of liquid polydimethylsiloxane and some solid iodine were put into a 100 ml triangle glass flask with a ground stopper. The flask was set in a thermostat and its temperature was controlled at $25 \pm 0.5^\circ\text{C}$. The contents of the flask were agitated by a magnetic stirrer covered by Teflon. The stirrer was stopped to settle the solution intermittently, and the

* Received on June 23, 1972

〒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

Table 1 Physical properties of silicone oil ((poly)dimethylsiloxane)

Name of silicone oil	Molecular weight M	Number of silicon atoms in a molecule N_{Si}	Density d [g/cm ³]	Kinetic viscosity ν [cm ² /sec] $\times 10^2$
KF96L 0.65cs	162	2.0	0.753	0.65
1cs	225	2.9	0.818	1.00
2cs	375	4.9	0.873	2.00
5cs	740	9.8	0.915	5.00
KF96 10cs	1200	16.	0.935	10.0
50cs	5000	67.3	0.960	50.0
100cs	8800	117.	0.965	100.
1000cs	35000	470.	0.967	1000.

Table 2 Saturated concentration of iodine in ((poly)dimethylsiloxane (at 25°C))

Molecular weight M	Molar concentration C_1 [mol/l] $\times 10^2$	Mole fraction* $X_1 \times 10^2$	Volume fraction* $\phi_1 \times 10^3$
162	2.86	0.612	1.69
225	2.73	0.741	1.61
375	2.50	1.07	1.48
740	2.23	1.78	1.32
1200	2.35	2.94	1.39
5000	2.05	9.66	1.21
8800	2.14	16.3	1.26
35000	2.11	43.2	1.24

* Molar volume of iodine is 59 cm³/mol, and those of dimethylsiloxanes are listed in Table 3.

upper clean liquid part was sampled with a 5 ml whole pipette. The iodine concentration of the sampled solution was determined by titrating it with sodium thiosulphate aqueous standard solution. Aqueous solution of starch was used as indicator. The sampling and analysis procedures were repeated to reach an equilibrium value.

Before the sample solution was titrated, 5 ml or more of water was added to the sample to avoid the formation of a water-in-oil type emulsion during titration. If the sodium thiosulfate aqueous solution is dropped into agitated liquid oil without water, then the dropped aqueous solution makes very small-size droplets in the continuous oil phase. This is a fairly stable water-in-oil type emulsion, and it makes the titration less accurate. Further care was taken when the test liquid was highly viscous liquid polymer. In this case, liquid agitation by magnetic stirrer was continued more than 2 days running. Undissolved solid iodine in the viscous solution was settled by the use of a centrifugal machine (3000–4000 rpm). When the upper clean solution part was sampled by a pipette, the pipette was cleaned with a little cyclohexane, which is a good solvent for siloxane liquid, and this was added to the sampled solution. Cyclohexane acted also as a viscosity-reducing reagent.

Polydimethylsiloxane is a homologous series consisting of siloxane units: (-OSiMe₂-). The liquid polydimethyl-siloxanes used were: Shin-Etsu Silicone KF96L 0.65cs, 1cs, 2cs, 5cs, KF96 10cs, 50cs, 100cs and 1000cs. (Shin-etsu Chemical Co., Ltd.) Their mean molecular weight, density and viscosity are reported in a manual¹⁰⁾ (see **Table 1**). Iodine used was guaranteed grade, and water was ion-exchanged.

Fig. 1 Saturated iodine concentration in polydimethylsiloxane (PDS). Molar concentration C_1 , volume fraction ϕ_1 and mole fraction X_1 of iodine vs. kinetic viscosity ν of PDS (25°C)

2. 2 Results

The experimental results are shown in **Table 2**. The saturated concentration C_1 , mole fraction X_1 and volume fraction ϕ_1 of iodine are plotted vs. kinetic viscosity ν in **Fig. 1**. Volume fraction ϕ_1 and ϕ_2 are defined by

$$\phi_1 = \frac{n_1 V_1}{n_1 V_1 + n_2 V_2}, \quad \phi_2 = \frac{n_2 V_2}{n_1 V_1 + n_2 V_2}$$

The molar concentration of iodine C_1 is related to mole fraction X_1 and volume fraction ϕ_1 as follows:

$$\phi_1 = V_1 C_1 / 10^3, \quad \phi_2 = V_2 C_2 / 10^3 = 1 - \phi_1 \quad (1)$$

$$X_1 = \frac{C_1}{C_1 + C_2} = \frac{1}{1 + (1/\phi_1 - 1)(V_1/V_2)} \quad (2)$$

3. Solubility Equations

In this section, a simple solubility equation is given which shows good agreement with the iodine solubility in liquid polydimethylsiloxane measured in the previous section. The solubility equation is given combining the regular solution theory and the Flory-Huggins treatment.

3. 1 Solubility equation for regular solution

When the liquid component 1 and 2 make a regular solution, the solubility equation is given as follows^{6,11)}:

$$RT \ln a_1 = V_1 \phi_1^2 (\delta_1 - \delta_2)^2 + RT \ln X_1 \quad (3)$$

where δ is solubility parameter (square root of cohesive energy density), and a_1 is relative activity of pure component 1.

The first term on the right-hand side is an enthalpy term and the second is an entropy term. The assumptions on which Eq.(3) is based are summarized as follows:

(i) No volume change of mixing $\Delta V^M \approx 0$. (ii) Bragg-William's approximation; namely the equal probability of pairs 1-1, 1-2, and 2-2. (iii) Geometric mean approximation for cohesive energy density: $\epsilon_{12} \approx (\epsilon_{11}\epsilon_{22})^{1/2}$. (iv) Entropy change of mixing is essentially the same as in the case of ideal solution, regardless of different molar volumes of component 1 and 2.

Ordinary non-polymeric solutions without specifically strong interaction are known to obey Eq.(3).

3. 2 Solubility equation for liquid chain polymer solution

In general, the solubility equation of a solute 1 in partially miscible liquid 2 is obtained as follows by the use of the thermodynamic equilibrium condition^{6,11)}.

$$RT \ln a_1 = \Delta G_1 = \Delta H_1 - T\Delta S_1 \quad (4)$$

where ΔH_1 and ΔS_1 are, respectively, partial molar enthalpy and entropy change of mixing. Therefore, the problem reduces to how these two terms are calculated on the basis of liquid polymer segment model.

Now, let component 1 and 2 represent, respectively, non-polymeric solute and long-chain polymer. If the polymer consists of completely freely oriented segments and the volume per segment unit is about the same as that of one molecule of component 1, then

$$V_1 = V_{seg}, \quad V_2 = N_{seg}V_{seg} = N_{seg}V_1 \quad (5)$$

where N_{seg} is the number of segment units in a polymer molecule.

For the calculation of partial molar entropy change ΔS_1 in polymer solution, we usually use the Flory-Huggins treatment^{3,6,11)} which calculates the number of possible lattice configurations for a mixture of polymer molecules occupying N_{seg} sites each and solute molecules occupying a single site. The result is as follows:

$$\Delta S_1 = -R \{ \ln \phi_1 + (1 - \phi_1)(1 - 1/N_{seg}) \} \quad (6)$$

To the contrary, the segmental behavior of polymer molecules is usually neglected for the calculation of partial molar enthalpy change ΔH_1 : that is, the regular solution theory is directly employed^{6,11)} supposing that the polymer solution, composed of small solvent molecules and long-chain polymer molecules, satisfies the assumptions summarized in section 3. 1. Then ΔH_1 reduces to $V_1(1 - \phi_1)^2(\delta_1 - \delta_p)^2$, and the solubility equation is given as follows^{6,11)}:

$$RT \ln a_1 = V_1(1 - \phi_1)^2(\delta_1 - \delta_p)^2 + RT \{ \ln \phi_1 + (1 - \phi_1)(1 - 1/N_{seg}) \} \quad (7)$$

It is not natural, however, to presume that assumptions (ii) and (iii) for a regular solution hold also in polymer solutions regardless of a hundred times as much difference in molecular size between the small solvent molecules and large polymer molecules. We should rather consider the role of constituent segments of polymer in enthalpy calculation as well. That is, it is among solvent molecules and segment units that we should take the regular solution assumptions. In this case, the partial molar enthalpy change of mixing ΔH_1 reduces to $V_1(1 - \phi_1)^2(\delta_1 - \delta_s)^2$, where the segment solubility parameter δ_s is defined as follows with geometric mean approximation of cohesive energy density:

$$\delta_1 = (\epsilon_{11})^{1/2}, \quad \delta_s = (\epsilon_{ss})^{1/2}, \quad \epsilon_{1s} \approx (\epsilon_{11}\epsilon_{ss})^{1/2} \quad (8)$$

Then the solubility equation is given as follows:

$$RT \ln a_1 = V_1(1 - \phi_1)^2(\delta_1 - \delta_s)^2 + RT \{ \ln \phi_1 + (1 - \phi_1)(1 - 1/N_{seg}) \} \quad (9)$$

If Eq.(9) is compared with experimental data, we can expect that a constant segment solubility parameter δ_s is obtained for chain polymers in a homologue series regardless of degree of polymerization, in the range of sufficiently large number of segment units in a polymer molecule. This prospective conclusion, however, cannot be obtained by the use of Eq.(7), in which solubility parameter δ_p for a whole polymer molecule is used. Although Eqs.(7) and (9) are of the same form, the physical meanings of δ_p and δ_s are quite different.

4. Discussion of the Solubility Equation for Liquid Polydimethylsiloxane

4. 1 Determination of segment solubility parameter δ_s by the use of solubility data

The saturated volume fraction ϕ_1 of iodine for each polydimethylsiloxane can be calculated from Eq.(1) by the use of solubility data C_1 described in section 2. Therefore, if the number of segment N_{seg} for each polydimethylsiloxane is given, segment solubility parameter δ_s can be obtained from Eq.(9). However, since the volume of segment unit is not yet known, the number of segment units in a polydimethylsiloxane cannot be given *a priori* for each poly-siloxane liquid. On the other hand, Eq.(9) is derived assuming that the molar volume of solute 1, V_1 , is equal to that of segment V_{seg} . Here, segment solubility parameter δ_s is calculated for two cases. In case I, the number of segments N_{seg} is defined as the ratio of molar volume of polymer and that of solvent ($=V_2/V_1$). In case II, the number of segments is defined as the number of silicone atoms in a polydimethylsiloxane molecule N_{Si} . Considering the reciprocal form of segment number N_{seg} in Eq.(9), the calculated segment solubility parameters δ_s for these two cases are expected to approach the same constant value when polymer length becomes great. The calculated results are shown in **Table 3**. It is obvious from the table that the segment solubility parameter δ_s for both cases is nearly constant ($\delta_s \doteq 7.5 \text{ cal}^{1/2}/\text{cm}^3/2$) for any polydimethylsiloxane, in particular for long-chain polymers. This fact appears to prove the validity of this treatment.

4. 2 Solubility parameter δ_2 calculated as regular solution

The solubility parameter δ_2 of liquid dimethylsiloxane as regular solution was calculated by the use of Eq.(3). The results are given in Table 3. In this case, the polysiloxane molecule is supposed to be a rigid large molecule without any segmental movement. When the molecular weight becomes large, the mole fraction X_1 of iodine (solute) grows very large even though the molar concentration C_1 stands still. Therefore, Eq.(3) cannot be used for high-polymer solutions.

On the contrary, low-molecular weight dimethylsiloxanes are likely typical regular solution liquid. (The color of iodine in (poly)dimethylsiloxane is violet. This means no existence of specific interaction

Table 3 Molar volume and solubility parameter of (poly)dimethylsiloxane

Molecular weight	Molar volume of polydimethylsiloxane V_2	Molar volume per siloxane unit V_2/N_{si}	Number of segments in a molecule based on iodine molar volume N_{seg}	Number of silicon atoms in a molecule N_{si}	Solubility parameter*			
					from Eq.(9)		from Eq.(3)	from Eq.(10)
					case I δ_s	case II δ_s	δ_2	δ_H
162	215	107.5	3.6	2.0	7.51	7.34	7.95	5.87
225	273	94	4.6	2.9	7.52	7.42	8.12	5.71
375	430	87.7	7.3	4.9	7.52	7.46	8.44	5.33
740	809	82.6	13.7	9.8	7.48	7.46	8.91	5.01
1200	1280	80.2	21.7	16	7.54	7.53	9.43	4.88
5000	5210	77.4	88	67.3	7.46	7.64	10.95	4.70
8800	9120	77.9	155	117	7.50	7.50	11.95	4.65
35000	36200	77.0	613	470	7.49	7.49	—	4.64

* The physical quantities of iodine at 25°C used for calculation are: $a_1=0.258$ [—], $\delta_1=14.1$ cal^{1/2}·cm^{3/2}, $V_1=59$ cm³/mol. These values are found in the Tables 7.2 and 8.4 in the book by Shinoda¹¹⁾.

Fig. 2 Saturated concentration of iodine C_1 vs. number of segments in a polydimethylsiloxane molecule N_{seg} (25°C)

between iodine and (poly)dimethylsiloxane.*) Therefore, solubility parameter δ_2 for $N_{si}=2$ siloxane liquid, that is $\delta_2=7.95$ cal^{1/2}/cm^{3/2}, will be a correct value.

4.3 Solubility parameter δ_H from latent heat of vaporization

In the regular solution theory, solubility parameter δ is defined^{6,11)} by $\delta^2=(\Delta H_{vap}-RT)/V$, where ΔH_{vap} is latent heat of vaporization. The latent heat of vaporization of dimethylsiloxane, ΔH_{vap} was calculated from vapor pressure measurement in 1946 by Wilcock¹⁴⁾. He claimed the latent heat of normal dimethylsiloxanes ($N_{si}=2-11$) was expressed by linear function as follows:

$$\Delta H_{vap} = 4.70 + 1.65N_{si} \quad [\text{kcal/mol}] \quad (\text{at } 25^\circ\text{C}) \quad (10)$$

The solubility parameter based on Eq.(10) was calculated and is given in Table 3. The solubility parameters δ_H thus obtained show smaller values than those calculated by Eq.(9), even in the non-polymeric region, in which Eq.(10) is valid. The solubility parameter determined from solubility data is considered

Fig. 3 Molar volume of a polydimethylsiloxane (PDS) molecule V_2 and that of a siloxane unit V_2/N_{si} vs. number of silicon atoms N_{si} in a PDS molecule (25°C)

to have a more sound basis for predicting solubility than that from thermal data. As for higher polymer region, considerable decrease of δ_H is seen. This indicates that Eq.(10) cannot be extrapolated to the high-polymer region.

4.4 Comparison of solubility equations and data

The solubility equations, Eq.(3) and Eq.(10), are plotted as C_1 vs. N_{seg} curve in Fig. 2 for each solubility parameter. The measured solubility data are also plotted in the figure. This shows fairly good agreement between the theory and the experimental result.

The solubility of iodine in liquid polymer decreases as the chain length of polymer increases until N_{seg} is about 10. This is the effect of entropy contribution. For larger N_{seg} than about 10, however, the entropy term is constant for any segment number. That is, the solubility remains nearly constant regardless of polymer chain length.

4.5 The size of segment unit

In the entropy calculation by the Flory-Huggins treatment (Eq.(9)), the size of completely freely oriented segment unit is assumed to be the same as that of solute. Let's examine whether this condition is satisfied or not.

* As far as iodine is concerned, the cases which involve solvation are readily distinguished from the regular, violet solutions by their red, yellow or brown colors⁶⁾.

The molar volume of iodine at 298°K is 59 cm³/mol¹¹⁾. On the other hand, molar volume of polydimethylsiloxane increases with molecular weight in a manner shown in Fig. 3. However, since the molar volume per silicon atom V/N_{Si} approaches a constant value of 77 cm³/mol, the size of siloxane unit is supposed to be 77 cm³/mol, provided the number of silicon atoms is sufficiently large. The difference between the molar volume of iodine and that of siloxane unit (-OSi(Me)₂-) is 25 to 30 per cent. It may be concluded from the discussion above that the size of freely oriented segment in polydimethylsiloxane is the same as that of siloxane unit.

This is also concluded for the diffusion coefficient behavior of iodine in liquid polydimethylsiloxane, which will be reported later¹³⁾. On the contrary, the size of flow unit calculated from the activation energy for viscous flow⁵⁾ for polydimethylsiloxane has been reported¹⁴⁾ to be 7 times as large as the siloxane unit.

4.6 Flory interaction parameter

We obtained Eq.(9) as a solubility equation for polymer solution in section 3.2. However, the Flory-Huggins solubility equation for polymer solution is frequently used in the form of the following equation by the use of the Flory interaction parameter $\chi^{3,6)}$.

$$RT \ln a_1 = RT \{ \chi(1 - \phi_1)^2 + \ln \phi_1 + (1 - \phi_1)(1 - 1/N_{seg}) \} \quad (11)$$

where $\chi = \chi_S + \chi_H$. χ_S is an entropy contribution part and χ_H an enthalpy part.

For most solid polymer-solvent systems, χ_S is a value of between 0.3–0.4¹²⁾ and is treated as a constant. On the other hand, χ_H is usually approximated to $\chi_H = (V_1/RT) (\delta_1 - \delta_2)^2$ by the direct use of regular solution theory. As we have seen in section 3.2, δ_2 should be replaced by δ_s .

When δ_2 is thus replaced, it is obvious that Eq.(9) corresponds to $\chi_S = 0$ in Eq.(11). This may be interpreted as follows. In general solid polymer solution, segment units are constrained in their free motion. Therefore, the assumption of completely freely oriented segment motion does not hold. To the contrary, polydimethylsiloxane is known by its peculiarly low energy of activation for segment motion compared with other organic compounds, e. g. normal paraffins^{5,8)}. In other words, polydimethylsiloxane is an ideal material for Eq.(9). Moreover, since the solubility parameter of iodine and siloxane are 14.1 and 7.5 cal^{1/2}/cm^{3/2}, the enthalpy term of Flory interaction parameter χ_H reduces to 4.3, which is sufficiently larger than the usual χ_S value pointed out above.

4.7 Solubility parameter of solid silicon polymer (silicon rubber)

The solubility parameter of solid silicon polymer (silicon rubber) has been reported⁴⁾ to be 7.3 cal^{1/2}/cm^{3/2} on the basis of swelling measurement. Considering the accuracy of swelling method as well as the effect of fillers in rubbers, the solubility parameter of silicon rubber may be regarded as nearly the same as that of

liquid siloxane high polymer ($\delta = 7.5$ cal^{1/2}/cm^{3/2}). In other words, the segment motion of silicon rubber is truly in liquid-like state.

4.8 Molar-attraction constant of siloxane unit

In Small's method¹²⁾ for estimating solubility parameter of polymer, the additive nature of $(EV)^{1/2}$ in a polymer molecule is used, where E is cohesive energy and $(EV)^{1/2}$ is called molar-attraction constant. In this method, the molar-attraction constant $(EV)_p^{1/2}$ of a compound molecule is obtained as the summation of the contributions of atomic and constitutive groups present in the compound molecule.

$$(EV)_p^{1/2} = \sum_i (EV)_i^{1/2} \quad (12)$$

Small¹²⁾ has calculated molar-attraction constants for several atomic and constitutive groups using thermal data in the literature. However, those for silicon compounds are not listed. We obtain $(E_{seg} V_{seg})^{1/2} = 580\text{--}600$ cal^{1/2}.cm^{3/2}/mol as the molar-attraction constant for siloxane unit (-OSi(Me)₂-) by the use of its solubility parameter as determined in this work. When the contributions of methyl and oxygen group¹²⁾, which are respectively 214 and 70 cal^{1/2}.cm^{3/2}/mol, are subtracted from this value, the reduced value of 82–102 cal^{1/2}.cm^{3/2}/mol is obtained as the contribution of a silicon atom.

5. Conclusion

- (1) The solubility of iodine in polydimethylsiloxanes of varying degree of polymerization (number of silicon atoms), from 2 to 470, has been measured.
- (2) The data obtained show good agreement with a solubility equation derived on the basis that a polydimethylsiloxane molecule is composed of a certain number of completely freely oriented segments and that the mixture of these segments and iodine can be treated as a regular solution as far as enthalpy calculation is concerned.
- (3) A constant segment solubility parameter δ_s , which is about 7.5 cal^{1/2}/cm^{3/2}, is obtained regardless of degree of polymerization by the use of this solubility equation. This value is nearly the same as that of silicon rubber from swelling data.
- (4) On the basis of the discussion above, it is concluded that the size of a segment unit is nearly equal to that of a siloxane unit.
- (5) The molar-attraction constant for siloxane unit is found to be 580–600 cal^{1/2}.cm^{3/2}/mol.

Acknowledgement

The authors wish to express their appreciation for the support of this work by the Asahi Glass Foundation for the Contribution to Industrial Technology.

Nomenclature

a_1	= relative activity of component 1	[—]
C	= molar concentration	[mol/l]
d	= density	[g/cm ³]
E	= cohesive energy	[cal/mol]

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	

Literature Cited

- 1) Blanks, R. F. and J. M. Prausnitz: *Ind. Eng. Chem., Fundamentals*, **3**, 1 (1964)
- 2) Burrell, H.: *Official Digest*, **27**, 726 (1955)
- 3) Flory, P. J.: "Principles of Polymer Chemistry", Cornell Univ. Press, N. Y. (1953)
- 4) Fujii, M. (Ed.): "High Polymer Engineering, vol. XIII, Properties and Uses of Polymer(I)", Chijin-shokan, Tokyo (1969)
- 5) Glasstone, S., Laidler, K. J. and H. Eyring: "The Theory of Rate Processes", McGraw-Hill, N. Y. (1941)
- 6) Hildebrand, J. H. and R. L. Scott: "Solubility of Non-electrolytes", Reinhold Publ. Corp. (1950); Hildebrand, J. H., J. M. Prausnitz and R. L. Scott: "Regular and Related Solutions", van Nostrand Reinhold (1970)
- 7) Lieberman, E. P.: *Official Digest*, **34**, 30 (1962)
- 8) Rochow E. G.: "An Introduction to the Chemistry of the Silicones", John Wiley & Sons Inc. N. Y. (1951)
- 9) Scott, R. and M. Magat: *J. Polymer Sci.*, **4**, 553 (1949)
- 10) Shin-etsu Silicone Manual P6-3A; Shin-Etsu Silicon Technical Data T6-4
- 11) Shinoda, K.: "Solution and Solubility", Maruzen, Tokyo (1966)
- 12) Small, P. A.: *J. Appl. Chem.*, **3**, 71 (1953)
- 13) Watanabe, H. and T. Miyauchi: to be submitted
- 14) Wilcock, D. F.: *J. Am. Chem. Soc.*, **68**, 691 (1946)

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

* Received on July 28, 1972

〒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