

Correlation between equation of state and temperature and pressure dependence of self-diffusion coefficient of polymers and simple liquids

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Correlation between the equation of state and the temperature dependence of the self-diffusion coefficient D for polymers such as polystyrene (PS) and polydimethyl siloxane (PDMS) and simple liquids such as argon, methane and benzene and the pressure dependence of D for oligomers such as dimethyl siloxane (DMS) and simple liquids such as cyclohexane and methanol has been examined based on the equation of state derived previously. The experimental data used were published by Antonietti *et al.* and McCall *et al.* for polymers, by McCall for linear dimethylsiloxanes and by Jonas *et al.* and Woolf *et al.* for simple liquids. The expression for D in this work is given by

$$\ln(D/T) = A_1(M) - B_1\{(T_c - T)/T\}^{n_1} - C_1(T)\{P + P_1(T)\}^{m_1}$$

where $A_1(M)$ is a function of molecular weight M_w , $C_1(T)$ and $P_1(T)$ are functions of temperature and B_1 , n_1 and m_1 are constants determined experimentally. For simple liquids, the values of n_1 obtained range from 0.3 to 1.2, with an average $\bar{n}_1 = 0.76$, and m_1 is in the range 0.5–1.2, with $\bar{m}_1 = 0.79$. For polymers, values of n_1 are in the range 2.5–7.0 for PS and 0.5–1.3 for PDMS and m_1 for DMS is in the range 0.8–1.0. The relation $D\eta/T = f(M)$ is found to be useful for simple liquids over a wide range of temperature including the critical region and for pressures up to ≈ 5 kbar†. There is a close correlation between $\ln(D/T)$ and α_p and β_T through $\ln(D/T) \sim \ln D_c - \alpha_p^{-1} - \beta_T^{-1}$, where D_c is D at the critical temperature and α_p and β_T are the thermal expansion coefficient and compressibility, respectively. The molecular weight dependence of D for polymers and simple liquids is discussed based on the experimental data and recent theory of Doi and Edwards. A new model for the mechanism of self-diffusion in the liquid state is proposed.

(Keywords: self-diffusion coefficient; polymer; simple liquid; equation of state; Stokes–Einstein equation)

INTRODUCTION

The self-diffusion coefficient in the liquid state for polymers and simple liquids is the most fundamental quantity in understanding transport phenomena on the molecular level, and its temperature and pressure dependence is practically important. The Stokes–Einstein equation is a well known and important equation used in discussing the diffusion phenomena of spherical molecules in dilute solution, and is given by

$$D = kT/6\pi\eta a \quad (1)$$

where k is the Boltzmann constant, η the viscosity and a the diameter of the particle. The validity of equation (1) is shown by the extensive data available for simple liquids over a wide range of temperature and pressure^{1–8}. On the other hand, deviation from the Stokes–Einstein equation is also reported^{9–11}, given by

$$D \propto \eta^{-\alpha} \quad (2)$$

where $\alpha < 1.0$, e.g. $\alpha = 0.68$ (Reference 10). One of the explanations for equation (2) is discussed by Zwanzig *et al.*¹¹.

There has been extensive theoretical work on self-diffusion in the liquid state. Eyring *et al.*¹² derived the

equation $\ln D \propto -E_a/kT$, where E_a is the activation energy in the theory of absolute reaction rates. Cohen and Turnbull¹³ derived $\ln D \propto -v^*/v_f$ based on the free volume theory, where v^* is the critical volume and v_f the free volume. By assuming exponential decay of the autocorrelation function for the velocity of a particle, Longuet-Higgins and Pople derived an expression for self-diffusion¹⁴. Rigorous calculations of the self-diffusion coefficient by using the pair potential and distribution function have been done by Kirkwood *et al.*¹⁵ and Chapman and Cowling¹⁶. The behaviour of D in the critical region is discussed by Kawasaki¹⁷.

The main purpose of this work is to establish an empirical equation for D which can predict experimental data over a wide range of temperature, pressure and molecular weight and to discuss the Stokes–Einstein equation through a comparison of the empirical equation for $\ln D$ with that for $\ln \eta$ obtained previously¹⁸.

DERIVATION OF EMPIRICAL EQUATION FOR SELF-DIFFUSION COEFFICIENT

In previous work we derived an empirical equation for viscosity, expressed by¹⁸

$$\ln \eta = A_0(M) + B_0\{(T_c - T)/T\}^{n_0} + C_0(T)\{P + P_0(T)\}^{m_0} \quad (3)$$

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† 1 kbar = 100 MPa

where $A_0(M)$ is a function of the molecular weight of the liquid, $C_0(T)$ and $P_0(T)$ are functions of temperature and B_0 , n_0 and m_0 are constants determined by the experimental data. In this work we propose an empirical equation for D by analogy with equation (3):

$$\ln(D/T) = A_1(M) - B_1 \left\{ \frac{T_c - T}{T} \right\}^{n_1} - C_1(T) \{P + P_1(T)\}^{m_1} \quad (4)$$

In the special case $n_0 = n_1$, $m_0 = m_1$, $B_0 = B_1$, $C_0(T) = C_1(T)$ and $P_0(T) = P_1(T)$, equations (3) and (4) reduce to

$$\ln(D\eta/T) = A_0(M) + A_1(M) \quad (5)$$

which is the simplest relation between D and η . In a more general case, $n_0 = n_1$, $m_0 = m_1$, $P_0(T) = P_1(T)$, but $B_0 \neq B_1$ and $C_0(T) \neq C_1(T)$, it is derived that

$$\ln(D\eta^{(B_1/B_0)}/T) = C_1^* - C_2^* \{P + P_0(T)\}^{m_0} \quad (6)$$

where $C_1^* = A_1(M) + A_0(M) - B_1/B_0$ and $C_2^* = C_1 - C_0 B_1/B_0$, which corresponds to equation (2). For a polymer with large T_c , equation (4) reduces to

$$\ln(D/T) = A_1(M) - B_1 T^{-n_1} - C_1(T) \{P + P_1(T)\}^{m_1} \quad (7)$$

RESULTS

The temperature and pressure dependences of self-diffusion coefficients for polymers and simple liquids are shown in Figures 1–4. Linearity is observed, suggesting that equations (4) and (7) can predict the experimental data over a wide range of temperature and pressure. Sources of data, and indices and constants determined in this work, are listed in Tables 1 and 2. Values of n_1 in $\ln(D/T) \sim \{(T_c - T)/T\}^{n_1}$ are in the range 0.3–1.2 for simple liquids, 2.5–7.0 for PS and 0.5–1.3 for PDMS; values of m_1 in $\ln D \sim \{P + P_1(T)\}^{m_1}$ at constant temperature are 0.5–1.2 for simple liquids and 0.8–1.0 for DMS. Values of $A_1(M)$ are determined at atmospheric pressure, $P = 1$ bar, by using the approximation

$$A_1(M) = \ln(D/T) + B_1 \left\{ \frac{T_c - T}{T} \right\}^{n_1} + C_1(T) \{P + P_1(T)\}^{m_1} \sim \ln(D/T) + B_1 \left\{ \frac{T_c - T}{T} \right\}^{n_1} \quad (8)$$

where

$$C_1(T) \{P + P_1(T)\}^{m_1} \sim 10^{-3} \ll B_1 \left\{ \frac{T_c - T}{T} \right\}^{n_1}$$

at $P = 1$ bar is used.

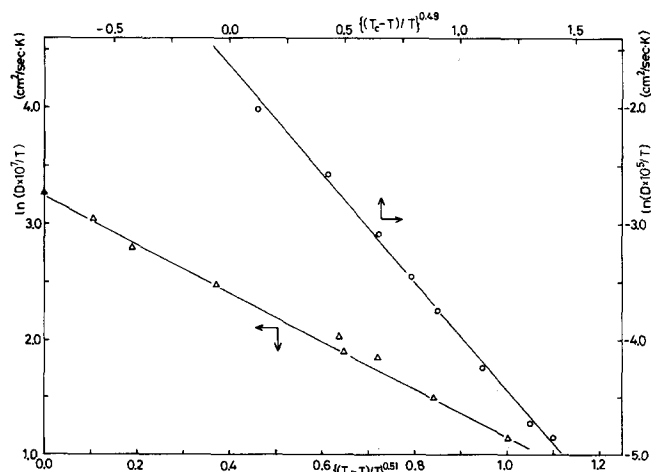


Figure 1 $\ln(D/T)$ versus $\{(T_c - T)/T\}^{n_1}$ for: Δ , methane with $n_1 = 0.51$; \circ , ethane with $n_1 = 0.49$. The unit of D is $\text{cm}^2 \text{s}^{-1}$

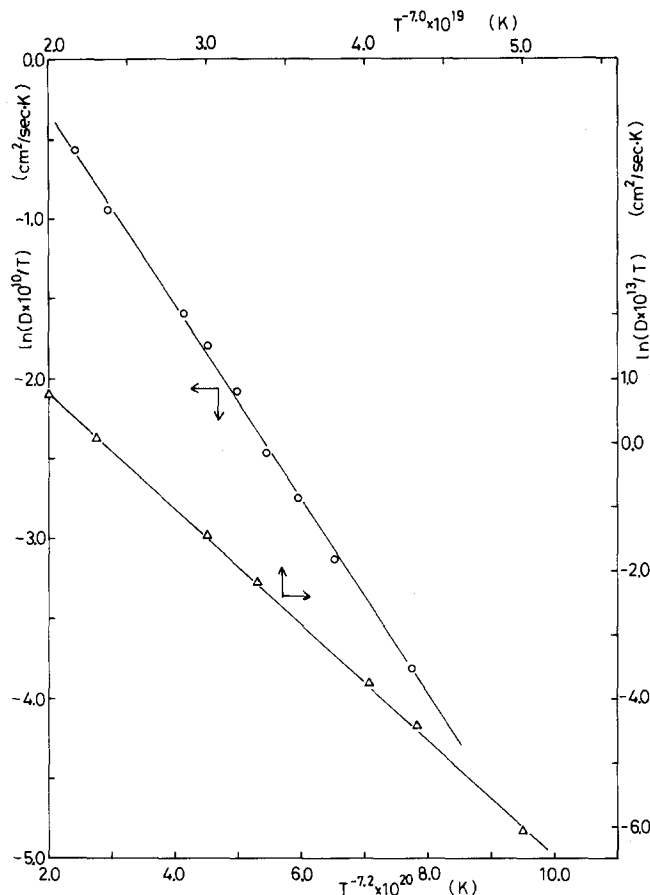


Figure 2 $\ln(D/T)$ versus T^{-n_1} for polystyrene: \circ , $M_w = 9200 \text{ g mol}^{-1}$, $n_1 = 7.2$; Δ , $M_w = 1.84 \times 10^4$, $n_1 = 7.0$

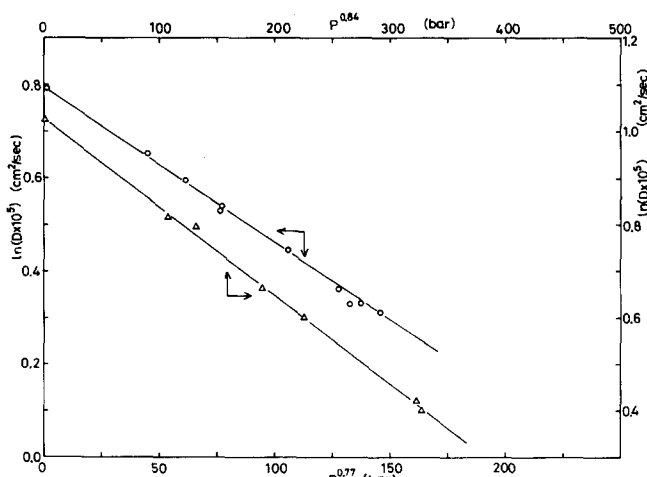


Figure 3 $\ln D$ versus P^{m_1} for benzene: \circ , 298.2 K, $m_1 = 0.77$; Δ , 313.2 K, $m_1 = 0.84$

DISCUSSION

It is interesting to compare quantitatively the expression for $\ln \eta$ in equation (3) with that for $\ln(D/T)$ in equation (4). In previous work we have obtained an expression for $\ln \eta$ (Reference 18). The temperature dependence of $\ln \eta$ and of $\ln(D/T)$ is examined through n_0 and B_0 for $\ln \eta$ and n_1 and B_1 for $\ln(D/T)$. For Ar, ethane and n-pentane n_0 in $\ln \eta$ is 0.5, $n_0 = 1.0$ for n-alkane, $9 \leq n \leq 64$, 7.0 for PS, 2.0 for PIB and 2.5 for polybutadiene¹⁸. For Ar n_1 is in the range 0.47–0.52, $n_1 = 0.49$ for ethane, $0.3 \leq n_1 \leq 1.2$ for n-alkane, $6 \leq n \leq 18$, and $2.5 \leq n_1 \leq 7.0$

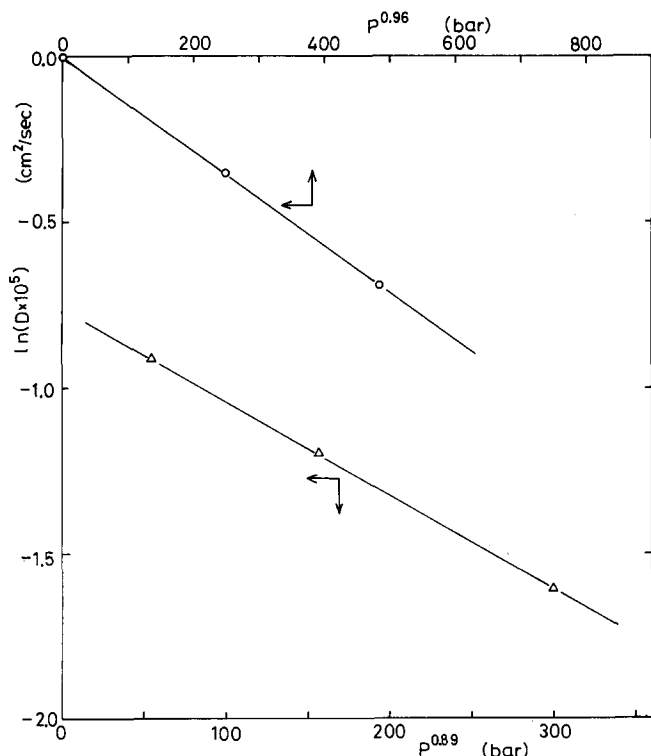


Figure 4 $\ln D$ versus P^{m_1} for dimethyl siloxane
 $(\text{CH}_3)_3\text{Si}\{\text{OSi}(\text{CH}_3)_2\}_{N-2}\text{OSi}(\text{CH}_3)_3$:
 \circ , $N=3$, $m_1=0.96$; \triangle , $N=5$, $m_1=0.89$

for PS. The average of B_0 in $\ln \eta$ is $\bar{B}_0=2.13$ in the simple liquids, compared with $\bar{B}_1=2.36$ in $\ln(D/T)$ (see Table 1). On the other hand, the pressure dependence of $\ln \eta$ and $\ln(D/T)$ is examined by m_0 , $C_0(T)$ and m_1 , $C_1(T)$. Values of m_0 for $\ln \eta$ in simple liquids except for CO_2 and H_2O are in the range 0.6–1.0, with $\bar{m}_0=0.79$, while m_1 in $\ln(D/T)$ is in the range 0.6–1.0 with $\bar{m}_1=0.79$. The constant C_0 is of the order of 10^{-3} , as is $C_1(T)$. Values of m_1 for water are almost equal to those of m_0 in $\ln \eta$ (see Table 2). From these quantitative comparisons between $\ln \eta$ in equation (3) and $\ln(D/T)$ in equation (4) the following relations are obtained:

$$n_0 \approx n_1 \quad (9a)$$

$$m_0 \approx m_1 \quad (9b)$$

$$B_0 \approx B_1 \quad (9c)$$

$$C_0 \approx C_1 \quad (9d)$$

These relations lead to equation (5) if $P_0(T)=P_1(T)$.

It is interesting to determine $A_1(M)$ in equation (4) through the experimental data. In this work we assume that

$$A_1(M) = A_1^* - \ln M_w^{a_i} \quad (10)$$

where A_1^* is a constant, $i=0$ for a simple liquid with $a_0=0.5$ and $i=1$ for a polymer with $a_1=0.0$. A plot of $A_1(M) + \ln M_w^{a_i} = A_1^*$ against $\ln M_w$ is shown in Figure 5, where A_1^* is in the range -11.5 to -13.0 for $\ln(D/T)$ with D in cm^3s^{-1} , which corresponds to 1.0×10^{-5} – 2.3×10^{-6} in D/T . For example, at $T=300\text{K}$, $3.04 \times 10^{-3} \lesssim D \lesssim 6.78 \times 10^{-4} \text{cm}^2\text{s}^{-1}$ which is comparable with the values for dense gas. As indicated in equation (4), $A_1(M)$ corresponds to $\ln(D/T)$ at the critical point if $P_1(T_c) = -P_c$ and is therefore nearly equal to that of gas.

A deviation from constancy occurs in Figure 5 for high molecular weights $M_w > 400$. Experimental data on the molecular weight dependence of D at constant T show that

$$D \sim M_w^{-\alpha} \quad (11)$$

where $2.0 \lesssim \alpha \lesssim 2.6$ (References 19–24), while the slope of A_1^* against $\ln M_w$ for high molecular weights in Figure 5 is ≈ -2.5 and $D \sim M_w^{-2.5}$.

It is important to discuss a correlation between the self-diffusion coefficient and the equation of state. It was found in previous work^{25,26} that the temperature dependence of the thermal expansion coefficient is given by

$$(\alpha_p T)^{-1} \sim X^{\beta_0} \quad (12)$$

$$\sim \{(T_c - T)/T\}^{\beta_0/3} \quad T \sim T_c \quad (13)$$

where X is defined by

$$X = (V_c - V)/V \quad (14)$$

and the pressure dependence of compressibility β_T is given by

$$\beta_T^{-1} \propto \{P + P_0^*(T)\}^{m_0^*} \quad (15)$$

where $\beta_0/3$ is in the range 0.67–1.0 for simple liquids if $2.0 \lesssim \beta_0 \lesssim 3.0$ and $0.7 \lesssim m_0^* \lesssim 1.0$ for polymers and simple liquids²⁶ with $\bar{m}_0^*=0.87$. From a comparison between $\ln(D/T)$ and equations (13) and (15), strong correlations are found between $\ln(D/T)$ and $-\beta_T^{-1}$ at constant temperature and $\ln(D/T)$ and $-(\alpha_p T)^{-1}$ at constant pressure. However, we cannot find such correlations in polymers as $n_1=7.0$ for PS. It is useful to express the

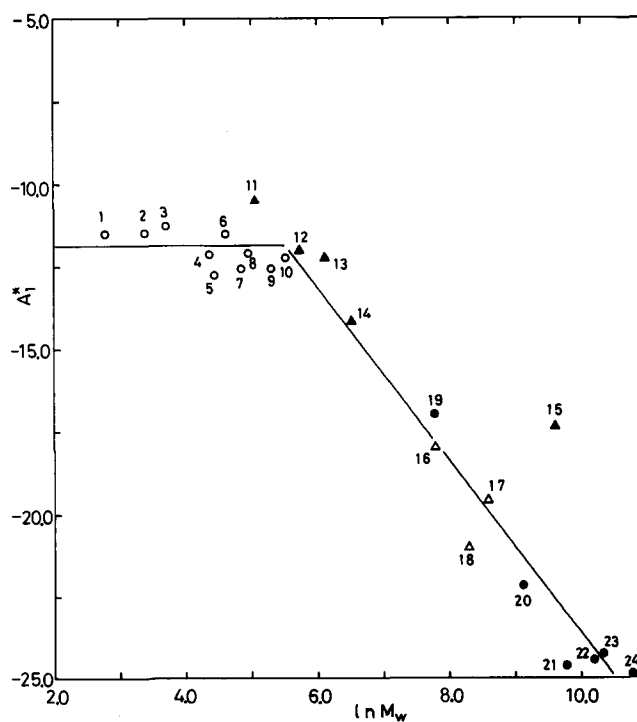


Figure 5 A_1^* versus $\ln M_w$ for polymers and simple liquids: 1, methane; 2, ethane; 3, Ar; 4, benzene; 5, n-hexane; 6, n-heptane; 7, n-nonane; 8, n-decane; 9, $\text{C}_6\text{H}_5\text{I}$; 10, n-octadecane; 11, DMS ($N=2$); 12, DMS ($N=4$); 13, DMS ($N=6$); 14, DMS ($N=9$); 15, PDMS, $M_w=1.5 \times 10^4$; 16, PE, $M_w=2440$; 17, PE, $M_w=5800$; 18, PE, $M_w=4100$; 19, PS, $M_w=2400$; 20, PS, $M_w=9200$; 21, PS, $M_w=18400$; 22, PS, $M_w=27100$; 23, PS, $M_w=31200$; 24, PS, $M_w=48400$

Table 1 Indices and constants in $\ln(D/T) = A_1(M) - B_1\{(T_c - T)/T\}^{n_1} - C_1(T)\{P + P_1(T)\}^{m_1}$ for polymers and simple liquids^a

Liquid	n_1	B_1	$-A_1(M)$	Temp. range (K)	Ref.
Argon	0.52	3.05	13.14	85–115	39
	0.47	2.93	13.08	90.4–150.7	40
Methane	0.51	2.08	12.88	94.9–183.7	41
	0.60	2.16	12.98	95–182.5	42
Ethane	0.49	2.30	13.17	101–301	43
n-Heptane	1.24	2.66	13.81	194–369	44
n-Nonane	1.12	1.67	15.00	212–421	45
n-Decane	0.83	2.16	14.59	322–477	45
n-C ₁₈ H ₃₆	0.99	2.34	15.02	315–418	46
Benzene	0.79	2.18	14.34	337–562	9
C ₆ H ₅ I	1.16	1.32	15.28	242–445	46
n-Hexane	0.38	3.45	14.97	276–506	45

Polymer	n_1	B'_1	$-A_1(M)$	Temp. range (K)	$10^{-4}M_w$	Ref.
PS	7.0	2.25×10^{19}	24.63	410–468	1.84	20
	6.5	1.18×10^{18}	24.46	414–474	2.71	20
	6.1	1.10×10^{17}	24.24	415–478	3.12	20
	5.9	3.36×10^{16}	24.93	420–482	4.84	20
	3.5	2.46×10^{10}	20.75	422–472	7.23	20
	2.5	7.7×10^7	17.23	435–484	16.1	20
	2.8	1.86×10^8	20.22	423–532	0.24	35
	7.2	6.09×10^{19}	22.13	451–530	0.92	35
PE	2.1	9.13×10^5	20.94	397–487	0.244	35
	1.0	2.69×10^3	19.58	411–468	0.58	34
DMS	0.67	2.68×10^2	10.51	290–336	0.0162	47
	0.50	1.5×10^2	8.36	271–330	0.0237	47
	0.85	7.0×10^2	12.02	270–316	0.0311	47
	0.90	1.0×10^3	12.20	268–335	0.0459	47
	1.25	5.85×10^3	14.16	237–340	0.0682	47
PDMS	1.10	3.2×10^3	17.28	323–435	1.50	33

	n_1	B_1	$-A_1(M)$	Temp. range (K)	Ref.
Water	1.94	1.444	16.48	273–373	9
	0.695	1.773	17.77	473–623	9

^a The unit of D is $\text{cm}^2 \text{s}^{-1}$

correlation by

$$\ln(D/T) = \{\ln(D/T)\}_c - k_0(\alpha_p T)^{-1} - k_1 \beta_T^{-1} \quad (16)$$

The physical meaning of $\ln(D/T)$ in equation (16) is attributed to that of $(\alpha_p T)^{-1}$ and β_T^{-1} . The quantity $(\alpha_p T)^{-1}$ means a variation of thermal energy $k\Delta T/kT$ due to a change of volume $\Delta V/V$, which comes from $(\alpha_p T)^{-1} = (\partial \ln T / \partial \ln V)_P$, while $\beta_T^{-1} = (\partial P / \partial \ln V)_T$ gives a pressure change ΔP associated with $\Delta V/V$ at constant temperature and gives a measure of variation of mechanical energy due to volume change. One can say that $(\alpha_p T)^{-1}$ and β_T^{-1} are related to the variation of energy associated with the volume change. It is interesting to note that the temperature and pressure derivatives of Gibbs free energy are related to α_p and β_T as follows:

$$(\partial G / \partial V)_T = -\beta_T^{-1} \quad (17)$$

and

$$(\partial G / \partial V)_P = -(S/V)\alpha_p^{-1} \quad (18)$$

These mean that the Gibbs free energy increases with decreasing volume and $|\Delta G|$ is larger in a liquid with smaller α_p and smaller β_T . In the diffusion process of a liquid, collisions between molecules occur frequently and the diffusing molecule loses energy in the form of mechanical work and heat. The terms $(\alpha_p T)^{-1}$ and β_T^{-1} in equation (16) may reflect the negative contribution to the self-diffusion coefficient due to collisions, which disappear in a dilute gas where $\ln(D/T) \sim A_1(M)$ in equation (4). Some data supporting equation (16) are shown in water, where the pressure dependence of $(\alpha_p T)^{-1}$ (Reference 27) indicates a maximum at a lower temperature $T = 25^\circ\text{C}$ and a monotonous decrease with pressure for the higher temperature $T = 50^\circ\text{C}$, as shown in Figure 6, which is comparable with the pressure dependence of $\ln(D/T)$ (Reference 28).

The theoretical work on D is very interesting. Litovitz *et al.*²⁹ proposed that mobility of molecules depends upon two independent processes: the occurrence of a sufficiently large vacancy near a molecule and the

Table 2 Indices and constants in $\ln(D \times 10^5) = f_0(T) - C_1(T)(P + P_1)^{m_1}$ for polymers and simple liquids^a

Liquid	m_1	P_1 (bar)	T (K)	$f_0(T)$	$10^3 C_1(T)$	Max. P (bar)	Ref.
Methanol	0.855	0	263.0	0.825	0.825	4365	48
	0.788	0	283.0	0.516	1.28	4905	48
	0.779	0	298.2	0.887	1.30	3858	48
	0.828	0	303.0	1.01	0.904	4905	48
Ethanol	0.645	0	298.2	0.096	5.24	2652	49
Benzene	0.770	0	298.2	0.794	3.32	645	4
	0.842	0	313.2	1.029	1.91	975	4
	0.762	0	328.2	1.300	3.09	1496	4
	0.860	0	333.2	1.308	1.68	1544	4
	0.670	0	348.0	1.496	7.40	2958	4
	0.722	0	393.3	1.950	4.50	4544	4
Tetramethyl siloxane (TMS)	0.538	0	433.0	2.61	23.2	4000	4
	0.724	0	298.0	1.38	6.17	4000	4
TMS	0.620	0	323.0	1.865	14.9	4000	4
	0.584	0	348.9	2.15	19.2	4500	4
Methyl cyclohexane	0.532	0	373.0	2.54	31.5	4500	4
	0.790	0	203.0	-1.76	5.08	3000	50
	0.856	0	223.0	-1.17	3.04	4000	50
	0.740	0	253.0	0.065	7.15	5000	50
Cyclohexane	0.800	0	298.0	0.672	3.52	5000	50
	0.986	0	313.0	0.652	1.12	600	7
	0.849	0	333.0	1.018	2.78	1000	7
	0.688	0	358.0	1.469	8.97	1600	7
Carbon tetrachloride	0.738	0	383.0	1.77	6.05	2140	7
	0.777	0	298.2	0.413	4.75	1216	3
	0.677	0	313.2	0.537	7.67	1469	3
Methyl iodide	0.873	0	328.2	0.733	1.77	1475	3
	1.12	0	302.2	0.0	0.12	6000	2
	0.81	0	288.19	0.3745	1.85	2928	51
DDMF ^b	0.785	0	298.1	0.5433	2.22	2958	51
	1.02	0	313.15	0.603	2.88	2908	51
	0.90	0	288.15	-0.343	0.84	2588	51
NMF ^c	0.875	0	298.15	-0.162	0.95	2732	51
	0.92	0	313.15	0.133	0.64	2948	51
	0.841	0	323.0	-0.504	4.23	584	52
Water	0.841	0	323.0	-0.504	4.23	584	52
	1.10	-1000	277.2	0.312	1.33×10^{-2}	3018	28
	1.69	-1012	283.2	0.486	1.71×10^{-4}	3032	28
	1.34	-507	298.2	0.854	1.98×10^{-3}	3008	28
	1.37	0	318.2	1.268	1.59×10^{-3}	2998	28
Heavy water	0.89	0	333.2	1.544	7.7×10^{-2}	2940	28
	1.18	-2000	283.2	0.291	1.49×10^{-2}	6000	6
	1.39	-1000	303.2	0.725	3.50×10^{-3}	9000	6
	0.99	0	333.2	1.325	5.89×10^{-2}	8000	6
	0.981	0	363.2	1.724	7.96×10^{-2}	9000	6
	0.800	0	393.2	2.09	0.455	8000	6
	0.700	0	423.2	2.51	1.13	9000	6
	0.767	0	473.2	2.88	0.668	9000	6
DMS $N=3$	0.96	0	298.2	0.0	1.43	700	47
DMS $N=5$	0.89	0	298.2	-0.758	2.84	700	47

^a The unit of D is $\text{cm}^2 \text{s}^{-1}$ ^b N,N -dimethyl-1-[$^2\text{H}_1$]formamide^c N,N -dimethyl formamide^d Octamethylcyclotetrasiloxane

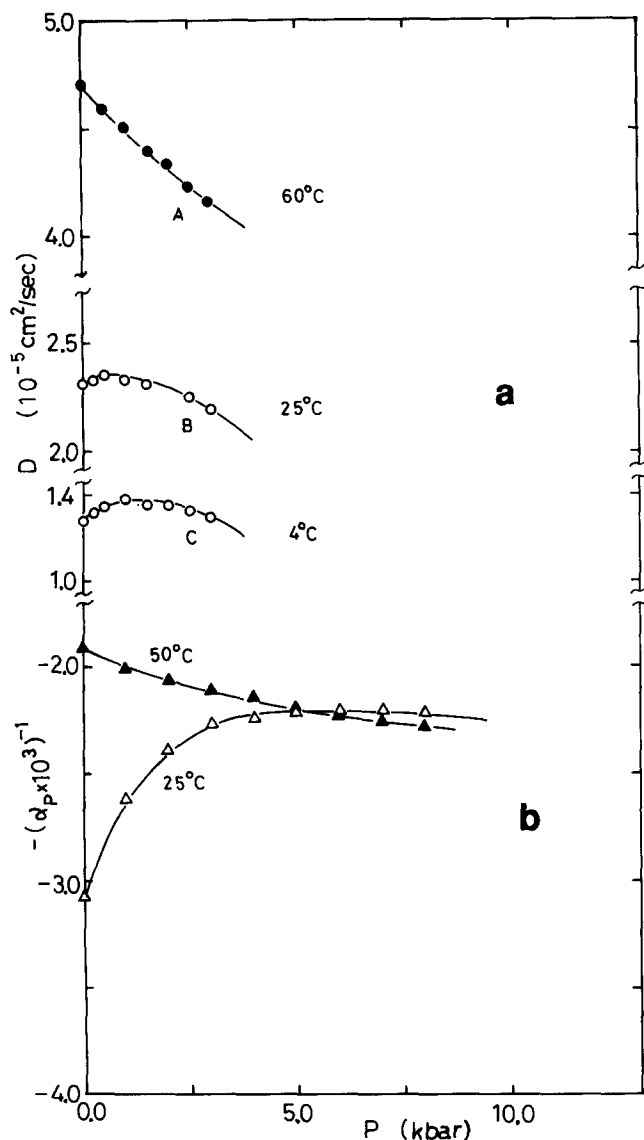


Figure 6 (a) D versus P for water at: A, 60°C; B, 25°C; C, 4°C. (b) $-\alpha_p^{-1}$ versus P for water at: \blacktriangle , 50°C; \triangle , 25°C

molecule itself gaining enough energy to break away from its neighbours. In the latter process a minimum energy loss is necessary. Cohen and Turnbull¹³ stressed the importance of the former process and assumed that a molecule can move into a vacancy only if it reaches a critical volume v^* by fluctuation and coalescence of the smaller free volumes of neighbouring molecules. The equation is given by

$$D = ga^*u \exp(-\gamma v^*/v_f) \quad (19)$$

where g is a geometric factor, a^* the molecular diameter and γ a numerical factor. Equation (19) is expressed as a function of temperature and pressure as follows:

$$\ln D \sim \{\bar{v}_m \bar{\alpha}_p (T - T_0) - \bar{v}_0 \bar{\beta}_T \Delta P\}^{-1} \quad (20)$$

where \bar{v}_m is the mean molecular volume, \bar{v}_p the mean molecular volume for the pressure increment ΔP , and $\bar{\alpha}_p$ and $\bar{\beta}_T$ are the mean thermal expansion and compressibility, respectively. Gray³⁰ pointed out that there is a significant probability that the molecule will jump back to its original position. He reviewed the statistical mechanics theory of the transport process, where the parameters of the pair potential and radial distribution

function and its density derivative are important, and stressed that great accuracy of these functions is needed to predict the experimental data³⁰. O'Reilly³¹ discussed the temperature and pressure dependence of D for water by the scaled particle theory, in which the work required to create a vacancy of molecular dimension is evaluated.

We tried to determine a volume dependence of $\ln(D/T)$ for simple liquids, expressed by

$$\ln D = A_2 X^{\delta_0} + B_2 \quad (21)$$

Values of δ_0 , A_2 and B_2 obtained from the data are shown in Table 3, where δ_0 is in the range of 1.0–5.0, with an average $\bar{\delta}_0 = 2.8$, and varies greatly with temperature.

Kawasaki¹⁷ shows that a large anomaly in D near T_c is not expected, but a sharp discontinuity in the first derivative of D versus temperature is expected. According to equation (16), there is no anomaly at T_c but $d \ln D/dT \sim -(T_c - T)^{-0.33} - (T_c - T)^{0.33}$ diverges at T_c , where $\alpha_p^{-1} \sim (T_c - T)^{0.67}$ and $\beta_T^{-1} \sim (T_c - T)^{1.33}$ obtained in the previous work are used^{25,26}.

It is very important to discuss the molecular weight dependence of D for polymers and simple liquids. It is found experimentally that $D \sim M^{-0.5}$ for compressed rare gases³², $D \sim Z^{-1.55}$ for polydimethyl siloxane³³ for $2 \leq Z \leq 284$, where Z is the number of silicone atoms per molecule; $D \sim n^{-1.67}$ for normal paraffin³⁴ for $7 \leq n \leq 400$; $D \sim M^{-2.4} - M^{-2.5}$ for polystyrene and poly(methyl styrene)²³ for $3.0 < 10^{-4} M_w < 15.0$ and $D \sim M_w^{-2.0}$ for $10^{-4} M_w > 15.0$; $D \sim M_w^{-2.0} - M_w^{-2.4}$ for PS; where the indices depend on temperature²⁰; $D \sim M_w^{-2.0}$ for PS and PE³⁵ above and below the critical molecular weight M_c ; $D \sim M_n^{-1}$ for polyethylene glycol for $M_n \leq 10^3$; and $D \sim M_n^{-2}$ for $M_n > 3 \times 10^3$ (Reference 19). On the other hand, the molecular weight dependence of viscosity η is given by $\eta \sim M_w^{0.5}$ for simple liquids over $M_w < 1000$, $\eta \sim M^{1.0}$ for polymers with $M_w < M_c$ and $\eta \sim M_w^{3.4}$ for the high molecular weight $M_w > M_c$ (Reference 18). It is shown from these results that $D\eta \sim M^0$ for simple compressed gas or liquid, $D\eta \sim M^{-0.5 \sim -1.2}$ for n-paraffin and oligomers, $D\eta \sim M^{-1.0}$ for polymers with $M_w < M_c$, and $D\eta \sim M_w^{1.0 \sim 1.4}$ for $M_w > M_c$. In Table 4 the contributions of terms in equation (3) for η and those in equation (4) are evaluated for polystyrene at $T \sim 490$ K where contributions from $(P + P_0)^{m_0}$ and $(P + P_1)^{m_1}$ are neglected at 1 bar. It is shown that the molecular weight dependent term in D , $A_1(M)$, is dominant over lower M_w and the $B_1 T^{-n_1}$ term reflecting a contribution from the local motion increases with increasing M_w and becomes comparable with $A_1(M)$ at $M_w = 1.61 \times 10^5$, while for η , the term $B_0 T^{-n_0}$ is almost constant against M_w and the

Table 3 Indices and constants in $\ln(D/T) = A_2 - B_2 X^{\delta_0}$ for liquids^a

Liquid	$-A_2$	B_2	δ_0	Temp. (K)	Ref.
Methyl cyclohexane	6.53	3.76	1.50	203.0	50
	10.5	1.58	2.06	223.0	50
	13.7	0.418	3.04	253.0	50
	14.9	0.161	3.72	298.0	50
Cyclohexane	11.0	2.83	1.16	358.0	7
	14.6	0.288	3.18	383.0	7
Benzene	15.1	0.048	4.71	433.0	4
	14.8	0.208	3.10	393.0	4
	14.7	0.243	3.05	348.0	4

^a The unit of D is $\text{cm}^2 \text{s}^{-1}$

Table 4 Relative contributions of terms in $\ln(D/T) \sim A_1(M) - B_1 T^{-n_1}$ and $\ln \eta = A_0(M) + B_0 T^{-n_0}$ for polystyrene^a at $T \approx 490$ K

$\ln(D/T)^b$				$\ln \eta^c$			
$10^{-3}M_w$	n_1	$A_1(M)$	$-B_1 T^{-n_1}$	$10^{-3}M_w$	n_0	$A_0(M)$	$B_0 T^{-n_0}$
18.4	7.0	-24.63	-3.32	3.7	7.0	-1.50	3.25
27.1	6.5	-24.46	-3.85	4.9	7.0	-1.18	1.20
31.2	6.1	-24.24	-4.28	25.7	7.0	0.86	3.39
48.4	5.9	-24.93	-4.51	32.2	7.0	1.62	3.25
72.3	3.5	-20.75	-9.45	80.0	7.0	4.00	3.44
161.0	2.5	-17.23	-14.5	134.0	7.0	6.0	3.34

^a $M_c \sim 22.0 \times 10^3$, estimated from Ref. 18

^b Reference 22

^c Reference 18

term $A_0(M)$ increases rapidly with increasing M_w and becomes larger than $B_0 T^{-n_0}$ for $M_w > 8.0 \times 10^4$.

It is also pointed out in Table 4 that the temperature dependence of $\ln \eta \sim B_0 T^{-n_0}$ is different from that of $\ln D \sim -B_1 T^{-n_1}$. For example, n_0 for η is constant, $n_0 = 7.0$, for $3.7 \leq 10^{-3} M_w \leq 134$, while n_1 for D decreases from 7.0 to 2.5 with increasing M_w for $18.4 \leq 10^{-3} M_w \leq 161$. This suggests a deviation from $D\eta/T \propto f(M)$ in the range of high molecular weight where $D\eta/T \propto f(M, T)$ or $D\eta^\alpha/T \propto f(M)$ with $\alpha \neq 1.0$. The empirical relation $D\eta^\alpha = \text{const.}$ is also found in the xenon-hydrocarbon system where $\alpha = 0.68$ (Reference 10). Zwanzig *et al.*¹¹ discussed the validity of the Stokes-Einstein equation by introducing an effective hydrodynamic radius which includes unusual microscopic interaction between a diffusing molecule and its environment in explaining the non-Stokes-Einstein behaviour $D\eta^\alpha = \text{const.}$ They stressed that the Einstein relation $D \sim kT/\xi$ is a direct consequence of linear response theory, independent of any mechanism for the friction ξ , and in the standard macroscopic hydrodynamics the dissipation is proportional to first power of viscosity of the fluid. However, for polymers, there is another important contribution to D , which is an entanglement between polymer chains in melts or solutions. According to the Doi-Edwards theory, the diffusion coefficient of the centre of gravity of the polymer D_G and steady state viscosity $\eta^*(0)$ are expressed by³⁶⁻³⁸

$$D_G \sim M^{-2} \rho^{-2\alpha' - \beta'} \quad (22)$$

and

$$\eta^*(0) \sim M^3 \rho^{4\alpha' + \beta' + 1} \quad (23)$$

where ρ is the mass concentration, and α' and β' are constants. It is estimated from equations (22) and (23) that there is no unique relation between D_G and $\eta^*(0)$ as the Stokes-Einstein equation except for $\rho \rightarrow 1$ at which $D_G \eta^*(0) \sim M^{1.0}$. If the Stokes-Einstein equation is applied to the polymer with $M_w > M_c$, the diameter of the particle, a , is proportional to M_w^{-1} . This unreasonable result also indicates that the Stokes-Einstein equation is not valid in the polymer.

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