

Correlation between the equation of state and the temperature and pressure dependence of viscosity in polymer and simple liquids

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A correlation between the equation of state and the temperature dependence of viscosity η in polymers such as polystyrene, polyisobutylene and polybutadiene, in melt and simple and oligomeric liquids such as argon, methane and n-hydrocarbons C_5 – C_{64} , and pressure dependence of η in polymer polymethyl methacrylate and simple liquids such as carbon dioxide, water and n-pentane, has been examined on the basis of the experimental data published by Fox and Flory^{18,19}, Colby, Fetters and Graessley²³, and Herrmann and Knappe⁵² for polymers and Bridgman³, Hubbard and Brown³² for simple and oligomeric liquids. An expression of η obtained is given by $\ln \eta = A_0(M) + B_0\{T_c - T\}/T^{n_0} + C(T)(P + P_0(T))^{m_0(T)}$ where $A_0(M)$ is a function of molecular weight, T_c is the critical temperature, $C(T)$, $P_0(T)$ and $m_0(T)$ are functions of temperature, B_0 and n_0 are constants, which are determined from the experimental data of η over the wide range of temperature, including the critical region, and pressure up to 1.2×10^4 kgf/cm² for simple liquids and water up to 8×10^3 kgf/cm². The molecular weight dependence of η at constant temperature and pressure is also examined over the wide range of molecular weight $10 < M_w < 10^6$ g/mol and is expressed by $\ln \eta = A^* + a_i \ln M_w$ for polymers ($i=1$) and simple liquids ($i=0$) with $a_0=0.5$ for simple liquids and $a_1=1.0$ for polymers except for high molecular weight polymers with $a_1=3.4$ where A^* is a constant around -11.0 . The weak divergence of η in the vicinity of T_c observed in simple liquids, such as carbon dioxide, has been discussed through the correlation between the P – η^{-1} – T relation and the P – V – T relation for simple liquid in the critical region. Comparison between the WLF equation and the equation obtained in this work has been made based on the experimental data of η for a glass-forming liquid.

(Keywords: equation of state; viscosity; simple liquids; $M^{3.4}$ law; critical exponent; WLF equation)

INTRODUCTION

It is observed experimentally that the viscosity η of liquids, including polymer in melt, decreases with increasing temperature in an empirical form as $\ln \eta = A + B/T^{(1+a)}$ where a is a constant and equal to zero in most of simple liquids¹ and $a=0$ – 10 in polymer in melt² and increases with increasing pressure at constant temperature with $(\partial \ln \eta / \partial P)_T \approx 10^{-3}$ kgf/cm² for polymer and simple liquids^{3,4}. However, even in simple liquids such as benzene a deviation from $\ln \eta \propto T^{-1}$ occurs specially in the vicinity of the gas–liquid critical temperature T_c where η drops quickly with approaching T_c (ref. 5). The temperature dependence of η is discussed by Andrade⁶, Eyring⁷, Doolittle⁸, Williams^{9,10}, Hildebrand^{11,12}, and others, where the functions of η are expressed in a more general form by $\eta = \eta(V)$ and $\eta = \eta(T)$. The former cannot predict a negative value of $(\partial \ln \eta / \partial T)_V$ observed in simple liquids over high pressure³, while the latter cannot predict the positive $(\partial \ln \eta / \partial P)_T$. Abe and Nagashima¹⁴ applied the principle of corresponding states to the viscosity using the reduced pair potential and derived an empirical universal equation $\ln \eta \sim \ln V + (1/2) \ln T$. On the other hand a correlation between the equation of state P – V – T and viscosity is discussed by many authors. Sanchez¹⁵ derived a theoretical relation between η and P – V – T for glass-forming liquids. Miller⁴ and Porter¹⁶ reviewed relationships between η and P – V – T properties and estimated variation of $(\partial \ln \eta / \partial P)_T$

with temperature. Utracki¹⁷ proposed a method of computation of the pressure effect on the melt viscosity of polymer. The other important issues concerning viscosity are the molecular weight dependence of the melt viscosity for linear polymers, which was first discovered by Fox and Flory^{18,19} and investigated by Bueche²⁰, de Gennes²¹, Graessley^{22,23} and Doi and Edwards^{24–26}, and the weak divergence of η in the vicinity of T_c in simple liquids^{27–29}.

In this work we propose an expression for η for polymer and simple liquids:

$$\ln \eta = f_0(M) + f_1(T) + f_2(P, T) \quad (1)$$

where $f_0(M)$ is a function of molecular weight of liquid and $f_1(T)$ and $f_2(P, T)$ are functions of temperature and pressure and temperature, respectively. A main purpose of this work is to determine the functions in equation (1), on the basis of the experimental data of η over the wide ranges of molecular weight, temperature and pressure, and through a correlation between the viscosity and the equation of state for polymer and simple liquids over the non-critical and critical region derived earlier^{30,31}.

A CORRELATION BETWEEN THE EQUATION OF STATE AND THE TEMPERATURE AND PRESSURE DEPENDENCE OF VISCOSITY

In 1943, Hubbard and Brown³² published the experi-

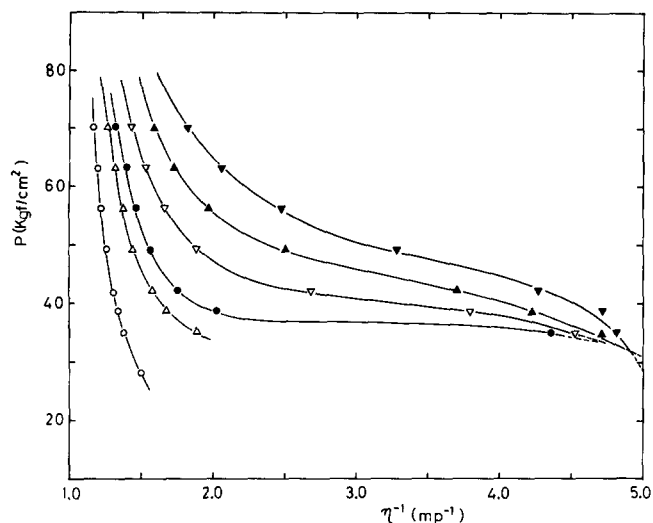


Figure 1 Pressure vs. η^{-1} (millipoise $^{-1}$) plot for n-pentane at various temperatures, (○), 180°C; (△), 195°C; (●), 200°C; (▽), 210°C; (▲), 220°C; (▼), 230°C ($T_c = 196.4^\circ\text{C}$; $P_c = 34.4 \text{ kgf/cm}^2$)

mental data of viscosity of n-pentane over the wide range of temperature and pressure including the critical region, which is replotted as pressure P against the inversed viscosity η^{-1} in Figure 1 where the $P-\eta^{-1}$ curve is almost the same as the $P-V$ curve in the equation of state at constant temperature, except for the regions of small η or large η^{-1} corresponding to the gas region where the $P-\eta^{-1}$ lines intersect each other so that η increases with increasing temperature in the gas region. In the $P-V$ isotherm, however, volume increases with increasing temperature in both gas and liquid regions. Therefore $P-V$ lines do not intersect in the gas region. From the rough correlation it can be determined that the functions of $f_1(T)$ and $f_2(P, T)$ in equation (1) based on the equation of state in the vicinity of the critical point.

A derivation of the semi-empirical equation of state in the noncritical and critical regions for polymer and simple liquids and related equations are given elsewhere^{30,31}. For example, the relation between the molar volume V and temperature is given by

$$(\alpha_p T)^{-1} = c_1 \{(V_c - V)/V\}^{\beta_0} \quad (2)$$

where α_p is the thermal expansion coefficient $\alpha_p = (\partial V/\partial T)_P/V$ and V_c is the critical volume, c_1 is a constant and equation (2) is expressed using an approximation $\int_{V_c}^V X^{\beta_0}/V dV = -AX^{n+1}$ by

$$\ln(T_c/T) = c_2 X^{n+1} \quad (3)$$

where X is defined by $X = (V_c - V)/V$ and β_0 , n and c_2 are constants.

From equation (3) in the vicinity of T_c

$$V_c/V = 1 + \{c_2^{-1} \ln(T_c/T)\}^{1/(n+1)} \quad (4)$$

and

$$\ln(V_c/V) \approx \{(T_c - T)/T\}^{1/(n+1)} \quad (5)$$

where $\ln(T_c/T) = (T_c - T)/T$ near T_c is used. The relation between V and P is given by³¹

$$\ln(V/V_0) = -D(T)\{P + P_0(T)\}^{(2\beta_0+1)^{-1}} + c_0(T) \quad (6)$$

where $c_0(T)$ is a function of temperature. From these facts about the $P-V-T$ relationship we propose the

following empirical equation of viscosity

$$\ln \eta = A_0(M) + B_0 \{(T_c - T)/T\}^{n_0} + C(T) \{P + P_0(T)\}^{m_0} \quad (7)$$

Equation (7) satisfies the conditions that $(\partial \ln \eta/\partial T)_P < 0$, $(\partial \ln \eta/\partial P)_T > 0$ and $(\partial \ln \eta/\partial T)_V < 0$ in the case where $n_0 > 0$, $m_0 > 0$, $B_0 > 0$ and $C(T) > 0$. For polymers where T_c is very high so that $(T_c - T)/T \approx T_c/T$, equation (7) is expressed by

$$\ln \eta = A_0(M) + B_1 T^{-n_0} + C(T) \{P + P_0(T)\}^{m_0} \quad (8)$$

RESULTS

Typical comparisons between the experimental data for η and calculated values from equations (7) and (8) are shown in Figures 2, 3 and 4. A linearity is observed in the plot of $\ln \eta$ vs. $\{(T_c - T)/T\}^{0.5}$ for n-pentane in Figure 2, $\ln \eta$ vs. $T^{-2.5}$ for polybutadiene in Figure 3, and $\log(\eta/\eta_0)$ vs. P^{m_0} for n-pentane in Figure 4 at temperatures of 30 and 75°C. A particular behaviour of

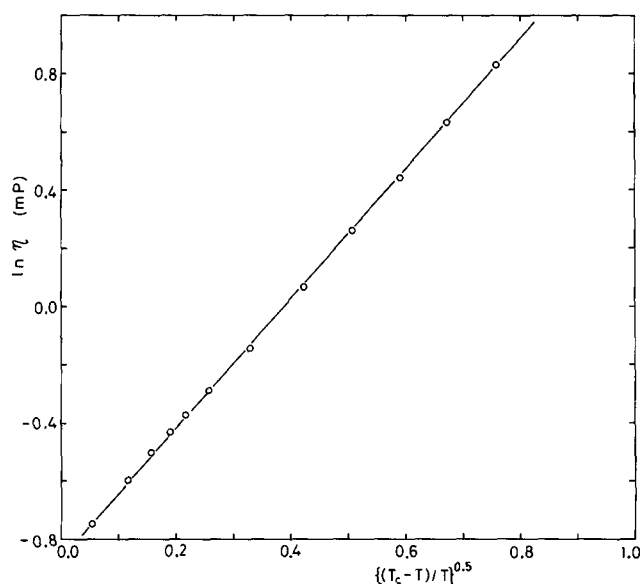


Figure 2 $\ln \eta$ vs. $\{(T_c - T)/T\}^{0.5}$ plot for n-pentane. η is in millipoises

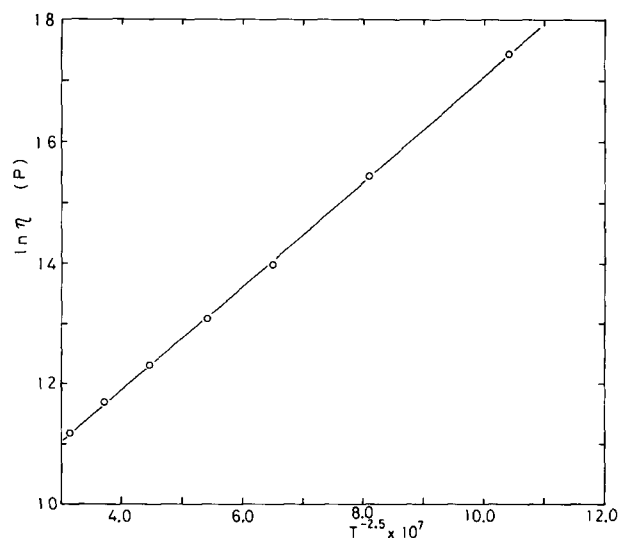


Figure 3 $\ln \eta$ vs. $T^{-2.5}$ plot for PBD with $M_w = 1.30 \times 10^5 \text{ g/mol}$. η is in poises

η against pressure for water at various temperatures is also predicted in Figure 5. The constants and indices in equations (7) and (8) determined by the best fitting with the experimental data of η are summarized in Tables 1, 2 and 3 where n_0 is the relationship of $\ln \eta \propto \{(T_c - T)/T\}^{n_0}$ is in the range of 0.5 to 1.0 for simple liquids and

oligomers and in the range of 2 to 3 for polymers, except for polystyrene with $n_0 = 7.0$. m_0 in $\ln \eta \propto \{P + P(T)\}^{m_0}$ is in the range of 0.6 to 1.0 for polymer and simple liquids, except for water where $m_0 = 1.2-1.7$ and CO_2 where $m_0 = 0.2-0.5$. It is also observed in Table 3 that m_0 is a decreasing function of temperature and $m_0 = m_0(T)$. Values of $A_0(M)$ in Tables 1 and 2 are determined from

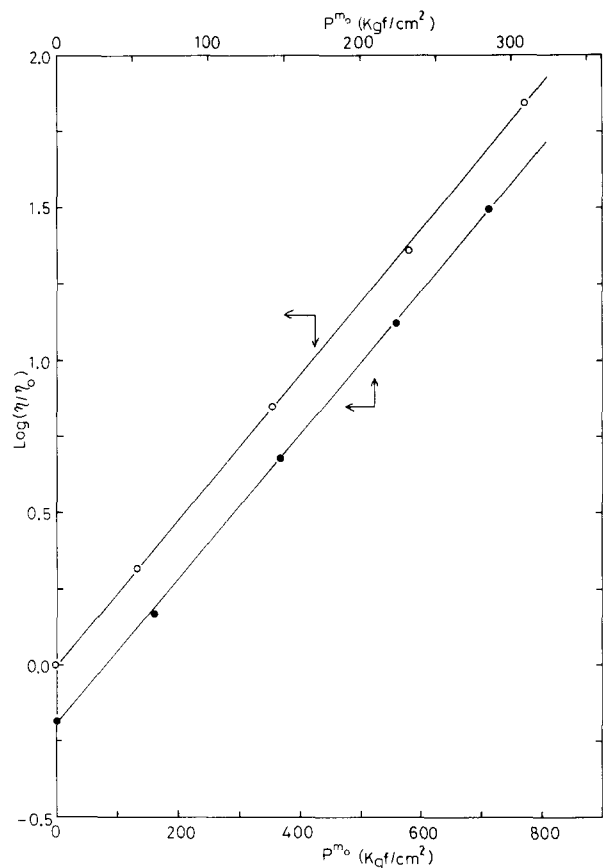


Figure 4 $\text{Log}(\eta/\eta_0)$ vs. P^{m_0} plot for n-pentane at various temperatures, (○), 30°C and (●), 75°C, where P is the pressure (kgf/cm^2). Value of $\eta_0 = 0.0022$ poise for n-pentane is that at 30°C and $P = 1 \text{ kgf}/\text{cm}^2$

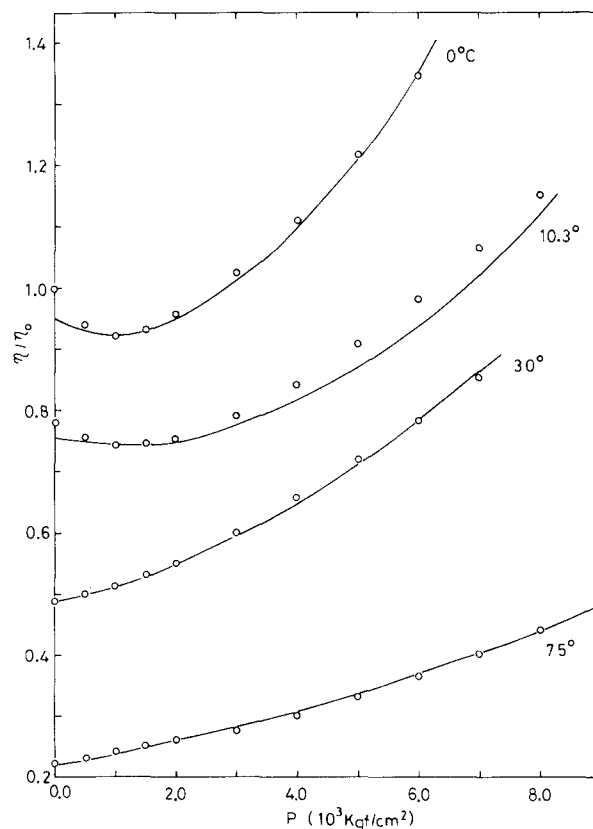


Figure 5 η/η_0 vs. pressure plot for water at various temperatures. The solid lines are calculated using equation (7) with constants in Table 3. (○), values observed

Table 1 Values of $A_0(M)$, A^* , n_0 and B_i in equations (7) and (8)

| Liquid ^a | $A_0(M)$ | A^* | n_0 | B_0 | Temperature range (°C) | Reference |
|---------------------|----------|-------|-------|----------------------|------------------------|---------------------|
| Ar | -7.85 | -9.69 | 0.50 | 2.14 | -188.9 to -124.2 | 48, 53 ^b |
| Methane | -7.67 | -9.05 | 1.0 | 1.34 | -182.2 to -93.2 | 48 |
| Ethane | -8.09 | -9.79 | 0.50 | 2.09 | -80 to 32.3 | 49 |
| n-Pentane | -7.78 | -9.92 | 0.50 | 2.24 | 25 to 195 | 32 |
| Benzene | -7.49 | -9.67 | 0.75 | 2.63 | 0 to 288.5 | 5 |
| C ₉ | -6.94 | -11.7 | 1.0 | 1.96 | -10.1 to 150.0 | 50 |
| C ₁₁ | -6.97 | -11.8 | 1.0 | 2.19 | -10.1 to 200 | 50 |
| C ₁₃ | -6.92 | -11.8 | 1.0 | 2.21 | -5.48 to 201.3 | 50 |
| C ₁₇ | -6.84 | -11.9 | 1.0 | 2.35 | 27 to 300.6 | 50 |
| Oligomer | | | | $B_1 \times 10^{-3}$ | | |
| C ₂₈ | -8.97 | -11.9 | 1.0 | 2.01 | 50 to 300.7 | 50 |
| C ₃₆ | -8.97 | -12.1 | 1.0 | 2.21 | 99.9 to 300.4 | 50 |
| C ₆₄ | -8.62 | -12.0 | 1.0 | 2.53 | 110.1 to 300.6 | 50 |
| | | | | B_1 | | |
| DMA | -1.80 | -10.2 | 2.2 | 2.61×10^6 | 82.4 to 201.5 | 51 |
| DEA | -3.98 | -10.8 | 3.0 | 1.99×10^8 | 0.2 to 167 | 51 |

^a The unit of η is poise

^b An intersecting point is observed in the isothermal η -pressure lines in argon, krypton and xenon

Table 2 Values of $A_0(M)$, A^* , B_1 , n_0 and $B_1 T^{-n_0}$ for polymers

| Polymer ^c | $A_0(M)$ | A^* | $B_1 \times 10^{-19}$ | n_0 | M_w (g/mol) | $B_1 T^{-n_0}$ | Temperature range (°C) |
|----------------------|----------|-------|-----------------------|-------|------------------|----------------|---------------------------|
| PS ^a | -1.50 | -9.72 | 0.568 | 7.0 | 3 700 | 3.25 | 53 to 138 |
| | -1.18 | -9.67 | 0.945 | 7.0 | 4 900 | 1.20 | 81.7 to 217 |
| | 0.86 | -9.29 | 2.30 | 7.0 | 25 700 | 3.39 | 156.5 to 217 |
| | 1.62 | -8.76 | 2.25 | 7.0 | 32 200 | 3.25 | 130 to 217 |
| | 4.00 | -7.29 | 2.36 | 7.0 | 80 000 | 3.44 | 178 to 217 |
| | 6.0 | -5.81 | 2.34 | 7.0 | 134 000 | 3.34 | 160 to 217 |
| | | | $B_1 \times 10^{-6}$ | | | | |
| PIB ^a | -3.35 | -12.7 | 1.25 | 2.0 | 11 200 | 5.22 | 6.45 to 217.2 |
| | -2.13 | -12.2 | 1.25 | 2.0 | 22 400 | 5.26 | 80.5 to 216.5 |
| | -0.685 | -11.2 | 1.31 | 2.0 | 38 200 | 5.46 | 155.6 to 217 |
| | 0.60 | -10.3 | 1.26 | 2.0 | 56 500 | 5.20 | 110 to 217 |
| | 2.23 | -9.06 | 1.18 | 2.0 | 80 000 | 4.78 | -9 to 217 |
| | 1.77 | -9.54 | 1.26 | 2.0 | 81 500 | 5.28 | 156 to 216.5 |
| | 8.65 | -4.75 | 1.18 | 2.0 | 660 000 | 4.89 | 8 to 217 |
| | | | $B_1 \times 10^{-6}$ | | | | |
| PBD ^b | -4.97 | -12.2 | 8.53 | 2.5 | 1 420 | 5.56 | -28 to 25 |
| | -4.18 | -11.8 | 8.38 | 2.5 | 2 120 | 5.47 | -28 to 25 |
| | -3.70 | -11.9 | 9.00 | 2.5 | 3 730 | 5.97 | -30 to 25 |
| | -3.13 | -11.4 | 8.50 | 2.5 | 4 030 | 5.62 | -30 to 25 |
| | -2.81 | -11.2 | 8.63 | 2.5 | 4 430 | 5.60 | -28 to 49 |
| | -0.50 | -9.76 | 8.60 | 2.5 | 10 500 | 5.64 | -30 to 49 |
| | 1.78 | -8.12 | 9.08 | 2.5 | 20 000 | 5.90 | -30 to 49 |
| | 4.65 | -6.09 | 9.00 | 2.5 | 46 000 | 5.82 | -51 to 73 |
| | 8.47 | -3.31 | 8.60 | 2.5 | 130 000 | 5.53 | -91 to 125 |

^a From ref. 18

^b From ref. 23

^c Unit of η for these polymers is poise

equations (7) and (8) by $A_0(M) = \ln \eta - B_0 \{(T_c - T)/T\}^{n_0} - C(T) \{P + P(T)\}^{m_0} \approx \ln \eta - B_0 \{(T_c - T)/T\}^{n_0}$ at 1 kgf/cm² where $C(T) \approx 10^{-3}$ and is negligible. Values of $A_0(M)$ are plotted against $\ln M_w$ in Figure 6 where $A_0(M)$ is characterized by $A_0(M) \sim M_w^{1.0}$ for M_w lower than the critical molecular weight M_c and $A_0(M) \sim M_w^{3.4}$ for $M_w > M_c$ where M_c is a molecular weight at which the $(\partial A_0(M)/\partial \ln M_w)_{T,P}$ changes from 1.0 to 3.4 with increasing M_w . It is speculated from Figure 6 that even in the polymer in melt $A_0(M)$ is less than zero over the lower molecular weight range and that there is a definite molecular weight of polymer at which $A_0(M) = 0.0$. The viscosity η is not influenced by the molecular weight of the polymer and is determined by the local motion of segments, which depends on temperature and pressure. The relative contribution of $A_0(M)$ and $B_1 T^{-n_0}$ to $\ln \eta$ for polymers is shown in Table 2 where B_1 is independent of the molecular weight of polymer, as is assumed in equation (8), and the contribution of $A_0(M)$ to $\ln \eta$ becomes larger with increasing M_w and dominant over the very high molecular weight of polymer compared to $B_1 T^{-n_0}$. The meaning of A^* in Tables 1 and 2 is discussed below.

DISCUSSION

It is very interesting to discuss the molecular weight dependence of η based on equations (7) and (8) and the experimental data of $A_0(M)$ in Figure 6. From equation

(7):

$$\ln \eta(T_c) = A_0(M) \quad (9)$$

Here an assumption that $P_0(T_c) = -P_c$ is used in equation (7) for η , which satisfies the case of $P-V$ for a simple liquid³¹ where P_c is the critical pressure. It is observed that $A_0(M) = -7.78$ for n-pentane (in poise) in Table 1 is nearly equal to $\ln \eta(T_c) = -7.78$ in poise or -0.87 in millipoise extrapolated to T_c in Figure 2. In the case of simple liquids $\ln \eta(T_c)$ is nearly equal to $\ln \eta_{\text{gas}}$ and may be expressed by¹

$$\ln \eta(T_c) \approx \ln \eta_{\text{gas}} = (1/2) \ln M_w + (1/2) \ln T + C \quad (10)$$

Although it is impossible to measure $\ln \eta(T_c)$ for a polymer, the limiting viscosity number $[\eta]$ in dilute solution gives some measure of η for an isolated polymer in gas, which is expressed by $[\eta] = M_w^{a^*}$ with $a^* = 0.5-1.0$. We use the free draining model of $[\eta] \approx M_w$ (refs. 33-35) or the Rouse model³⁶, which gives $\ln \eta(T_c) \sim \ln M_w$. The data in Figure 6 are replotted in Figure 7 using the relation

$$A_0(M) = A^* + \ln M_w^{a_i} \quad (11)$$

where A^* is a universal constant and $i=0$ for simple liquids with $a_0 = 0.5$ and $i=1$ for polymers with $a_1 = 1.0$. It is shown in Figure 7 that A^* is in the range of -10 and -12 corresponding to 4.5×10^{-5} to 6.1×10^{-6} in η . A deviation occurs over the high molecular weight indicated by $\eta \propto M_w^{3.4}$ in Figure 6, which may be

Table 3 Values of $C(T)$, $P_0(T)$, and $m_0(T)$ in equations (7) and (8)

| Liquid | t (°C) | $C(T) \times 10^3$ | $P_0(T)$ (kgf/cm ²) | $m_0(T)$ | Maximum pressure (kgf/cm ²) | Reference |
|--------------------------|-------------|----------------------|------------------------------------|----------|---|-----------|
| CO ₂ | 25.0 | 47.0 | -90 | 0.46 | 1 368 | 27 |
| | 29.9 | 289.0 | -58 | 0.265 | 958 | |
| | 31.1 | 63.1 | -105 | 0.425 | 1 464 | |
| H ₂ O | 0.0 | 1.1×10^{-3} | -1000 | 1.50 | 6 000 | 3 |
| | 10.3 | 1.2×10^{-3} | -1000 | 1.70 | 8 000 | |
| | 30.0 | 8.9×10^{-3} | 0 | 1.25 | 11 000 | |
| | 75.0 | 6.1×10^{-2} | 0 | 1.04 | 9 000 | |
| Ethanol | 30.0 | 3.06 | 0 | 0.739 | 12 000 | 3 |
| | 75.0 | 3.64 | 0 | 0.637 | 12 000 | |
| n-Propyl alcohol | 30.0 | 3.81 | 0 | 0.752 | 12 000 | 3 |
| | 75.0 | 6.43 | 0 | 0.678 | 12 000 | |
| n-Pentane | 30.0 | 5.48 | 0 | 0.708 | 12 000 | 3 |
| | 75.0 | 13.56 | 0 | 0.602 | 12 000 | |
| n-Hexane | 30.0 | 5.07 | 0 | 0.727 | 8 000 | 3 |
| | 75.0 | 4.64 | 0 | 0.652 | 12 000 | |
| Methylcyclohexane | 30.0 | 2.29 | 0 | 0.863 | 8 000 | 3 |
| | 75.0 | 3.01 | 0 | 0.818 | 12 000 | |
| Glycerin | 30.0 | 1.28 | 0 | 0.895 | 8 000 | 3 |
| | 75.0 | 1.52 | 0 | 0.844 | 12 000 | |
| Toluene | 30.0 | 0.99 | 0 | 0.922 | 8 000 | 3 |
| | 75.0 | 1.63 | 0 | 0.848 | 12 000 | |
| p-Cymene | 30.0 | 1.33 | 0 | 0.72 | 4 000 | 3 |
| | 75.0 | 0.97 | 0 | 0.732 | 8 000 | |
| PMMA ($M_w = 54\,000$) | 143.0 | 1.38 | 0 | 1.071 | 1 050 | 52 |
| | 154.0 | 1.96 | 0 | 1.00 | 1 050 | |
| | 166.0 | 6.90 | 0 | 0.802 | 1 050 | |

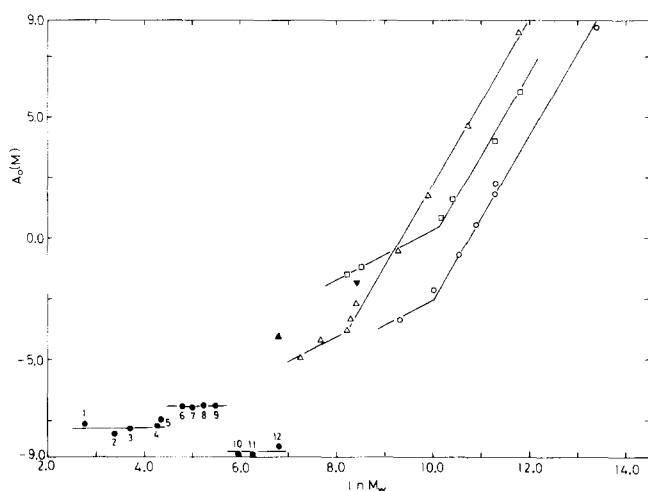
* 1 kgf/cm² = 0.9809 bar = 9.809 × 10⁴ Pa

Figure 6 $A_0(M)$ vs. $\ln M_w$ plot for simple liquids, oligomers and polymers (\square), polystyrene; (\circ), polyisobutylene; (\triangle), polybutadiene; (\blacktriangle), diethylene adipate $M_w=900$; (\blacktriangledown), decamethylene adipate polymer, $M_w=4510$. The numbers correspond to liquids such as (1), methane; (2), ethane; (3), argon; (4), n-pentane; (5), benzene, (6), C_9 ; (7), C_{11} ; (8), C_{13} ; (9), C_{17} ; (10), C_{28} ; (11), C_{36} ; (12), C_{64} . All values of $A_0(M)$ are obtained after corrections to poises

attributed to an extra contribution to $A_0(M)$ due to overlaps of polymer molecules in the melt state from that of a single polymer chain. Beuche²⁰ explained the extra term of $M_w^{2.4}$ by a sum of the contributions from the induced medium motion $M_w^{1.5}$ and the circulation motion $M_w^{1.0}$. A discussion critical to the Beuche theory is given by Graessley²². The effect of entanglement to η in a polymer in a melt is discussed by the reptation model of de Gennes²¹ and Doi and Edwards²⁴⁻²⁶ and by using Born-Green's method described by Chikahisa³⁷.

It is important to discuss the correlation between the equation of state and viscosity over the wide range of temperature and pressure including the critical region. Green³⁸ derived theoretically that the viscosity of liquid is effectively proportional to the radial distribution function at rest by taking into account the deformation of radial distribution function in the velocity gradient. It is interesting to compare the function of $P-V-T$ with that of $P-\eta^{-1}-T$. The relation between V and T is given by equation (5) $\ln(V_c/V) \propto \{(T_c - T)/T\}^{1/(n+1)}$, which can compare with equation (7) $\ln \eta \propto \{(T_c - T)/T\}^{n_0}$ with $n_0 = 0.5-1.0$ for simple liquids in Table I. In equation (5) $n = 2.0$ gives $\ln(V_c/V) \approx \{(T_c - T)/T\}^{0.33}$. The relation

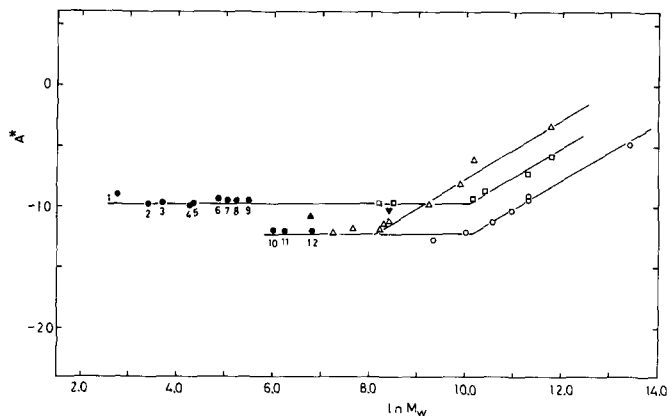


Figure 7 A^* vs. $\ln M_w$ plot for simple liquids, oligomers and polymers. The data are the same as those in Figure 6

between V and P is given by equation (6) with $\ln(V/V_0) \sim \{P + P_0(T)\}^{(2\beta_0+1)^{-1}} \sim \{P + P_0(T)\}^{0.2}$ with $\beta_0 = 2.0$, while $\ln \eta \sim \{P + P_0(T)\}^{m_0}$ with $m_0 = 0.6-1.0$.

The basic assumptions and conditions used in deriving equation (7) are as follows: equation (1); a correlation between η and V^{-1} ; a similarity between non-equilibrium properties with a divergence of fluctuation and correlation length near T_c and the correlated molecular motions in liquid under shear; the condition that η in liquid decreases with increasing temperature and η increases with temperature in gas. The last condition is satisfied in equation (7) if the variable X is redefined to include the gas region as $X = |(T_c - T)/T|$ because $\eta \sim (T - T_c)/T$ increases with temperature.

Bridgman proposed an interlocking mechanism of molecules in liquid between an adjacent layer to explain that the viscosity is not a function of volume only and the experimental result that η decreases with increasing temperature at constant volume³. According to the model, the number of interlocking molecules decreases with temperature and increases with pressure due to the probability of interlocking increases with decreasing molecular distance or volume, but decreases with increasing the thermal vibration of molecules or temperature, even at constant volume. This can explain $(\partial \ln \eta / \partial T)_V < 0$. The free volume theory on η stresses the fact that η decreases with temperature. This is only attributed to an increase of free volume, but in the interlocking mechanism this relationship is responsible for both increases of free volume and thermal vibration of molecules. Equation (7) is consistent with the interlocking mechanism where $\eta \sim \eta(T)$ at constant pressure and $\eta \sim \eta(P) = \eta(V)$ at constant temperature.

The physical meaning of indices such as β_0 in the $P-V-T$ relationship, n_0 and $m_0(T)$ in the $P-\eta^{-1}-T$ relationship and variables $X = (V_c - V)/V$ in the $P-V-T$ relationship and $(T_c - T)/T$ in the $P-\eta^{-1}-T$ relationship is of great importance. It is clear from the definition of $X = (V_c - V)/V$ that X expresses a number of molecules with volume V around a certain molecule over the volume of V_c . In this case the critical volume means the maximum range of interaction around the central molecule and the molecule is assumed to interact with molecules within the volume of V_c .

On the other hand the quantity $(T_c - T)/T = (k/2)(T_c - T)/(kT/2)$ in the $P-\eta^{-1}-T$ relationship expresses an extra energy of molecules per degree of freedom at T_c from that at T measured in a scale of $kT/2$. In both

variables, the gas-liquid critical point is considered as a reference point. The indices of β_0 and n_0 reflect a degree of influence of X and $(T_c - T)/T$ to the thermodynamic quantity such as α_P and η_c , respectively. Because we are mainly interested in the functional form of η estimated from data, a theoretical discussion on n_0 and $m(T)$ will not be given here. An introduction of T_c as a reference temperature in the viscosity of glass-forming liquid is discussed below.

The temperature dependence of $\log a_T \sim \log(\eta/\eta_g)$ for the glass forming liquids including polymers over the temperature range of the glass transition temperature T_g to $T_g + 100^\circ$ was discussed by Williams³⁹ and Williams, Landel and Ferry⁴⁰. This WLF equation is given by

$$\log a_T = C_1(T - T_g)/(C_2 + T - T_g) \quad (12)$$

Here a_T is a temperature 'shift factor' and C_1 , C_2 and $T_g \approx T_g + 50$ are constants. The WLF equation is expressed in a more simple form by using the Vogel equation

$$\ln \eta = \ln A + \{\alpha(T - T_0)\}^{-1} \quad (13)$$

where A , α and T_0 are constants⁴¹. Berry and Fox⁴¹ concluded, on the basis of the experimental data, that the Vogel equation does not represent data on a single liquid such as 1,3,5 tri-(α -naphthyl)-benzene over a wide range in temperature or wide range of η such as $\log \eta = 13.47$ to $\log \eta = -1.561$ in poise, although the equation is useful over the temperature range near T_g where the reference temperature is T_g . Examination of equation (7) in this paper for η of the glass forming liquids is shown in Figure 8, where a reasonable prediction is obtained over the temperature range measured for 1,3,5 tri-(α -naphthyl)-benzene⁴² and glucose⁴³ by using suitable values of T_c^* and n_0 determined by a best fit. The slope in the $\log \eta$ against $\{(T_c^* - T)/T\}^{n_0}$ for 1,3,5 tri-(α -naphthyl)-benzene changes from 8.9 over 69°C ($= T_g$) to 169°C ($= T_g + 100^\circ$) to 5.57 over 169°C to 310°C ($\approx T_g + 150^\circ$) but there is no change in the function of equation (7) with increasing temperature. Even in the case of polymer where T_c cannot be measured, equation (8) from equation (7) with $(T_c - T)/T \approx T_c/T$ is still useful (see Figure 3).

It is instructive to discuss the simplest expression for η

$$\eta^{-1} \sim (V - V_0) \quad (14)$$

which is derived by Batschinski⁴⁴ and Hildebrand¹¹. As was pointed out earlier, equation (14) cannot predict the observed values of $(\partial \ln \eta / \partial T)_V < 0$. The pressure dependence of η predicted by equation (14) is given by $(\partial \ln \eta / \partial P)_T \sim \{V/(V - V_0)\} \beta_T \sim P^{-0.8}$ and $\ln \eta \sim P^{0.2}$ or $(\partial \eta / \partial P)_T \sim \beta_T \times \{V/(V - V_0)\}^2 \sim \beta_T \sim P^{-0.8}$ and $\eta \sim P^{0.2}$, which are much slower than $\ln \eta \sim P$ or $\eta \sim P$ observed where a relation $\beta_T \sim P^{-0.8}$ obtained in the previous work is used³¹. The viscosity of liquid nitrogen, oxygen, argon and methane along isotherms up to 100 atm, measured by Hellems et al.⁴⁵, indicates that $\eta \sim P$.

The pressure dependence of η in polymer in melt is discussed by many authors. Miller⁴ has used a relation that $(\partial \ln \eta / \partial P)_T = -(\partial \ln \eta / \partial T)_P / (\partial T / \partial P)_\eta$. Penwell, Porter and Middleman⁴⁶ take into account (dT_g/dP) in the framework of the WLF equation to predict $(\partial \ln \eta / \partial P)_T$. Utracki used the hole fraction in the Doolittle formula for predicting $\eta(T, P)$ (refs. 17, 47).

Discussion on the weak divergence of viscosity at the

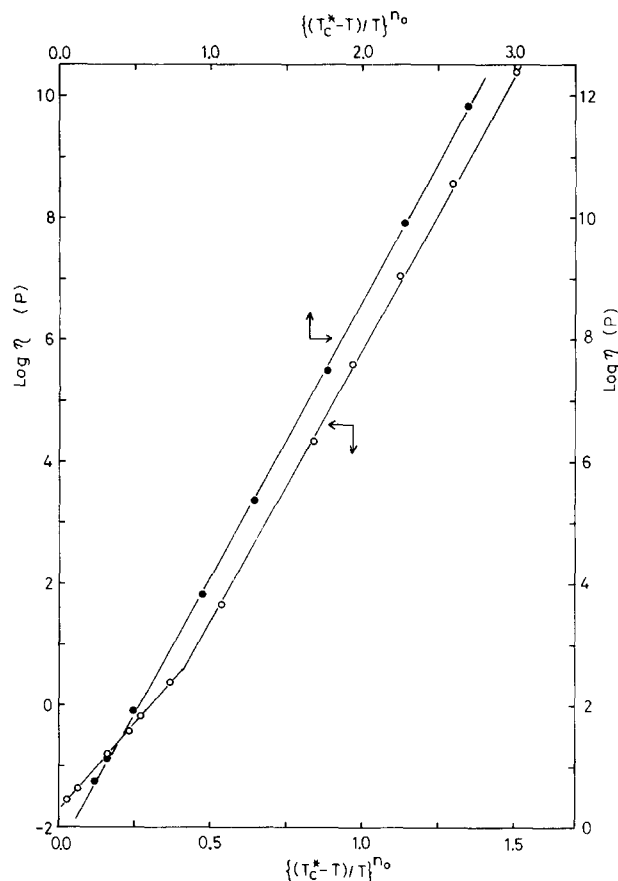


Figure 8 $\log \eta$ vs. $\{(T_c^* - T)/T\}^{n_0}$ plot for 1,3,5 tri-(α -naphthyl) benzene (\circ) and glucose (\bullet). The equation of η for 1,3,5 tri-(α -naphthyl)benzene is $\log \eta = 8.9 \{(750 - T)/T\}^{2.75} - 3.05$ over 69–169°C, $\log \eta = 5.67 \{(750 - T)/T\}^{2.75} - 1.72$ over 169–310°C, while $\log \eta = 4.45 \{(700 - T)/T\}^{3.68} - 0.30$ for glucose

critical point is also important. The data in *Figure 1* are replotted in *Figure 9* where η for n-pentane is plotted against temperature at constant pressure. A weak divergence of η is observed with approaching T_c from the higher along the isobar and isocore. This corresponds to the weak divergence of volume V in the V - P line of liquid under a constant temperature equal to T_c when pressure P approaches P_c from $P > P_c$. The dotted line in *Figure 9* indicates that η for the gas phase coexisted with the liquid phase and shows that η for gas increases with increasing temperature.

It is stressed here that equation (7) for η is very useful for polymers and simple liquids over a wide range of temperatures, including the glass transition temperature and the critical temperature, and pressures up to 12 kgf/cm², where the critical point is taken as a reference temperature and the result means that the basic equation (1) $\ln \eta = f_0(M) + f_1(T) + f_2(P, T)$ is valid. Equation (1) is consistent with $\eta = \eta(V)$ at constant pressure because $\eta(V)$ is expressed by a function of temperature at constant pressure and by a function of pressure at constant temperature. Although a correlation is found between η and V^{-1} in the P - V - T through the experimental data, that does not suggest a direct and simple relation of $\eta \propto V^{-1}$ because an essential difference between the P - η^{-1} - T and the P - V - T exists over the gas region. The uncorrelated behaviour between η and V^{-1} is reflected in the difference in indices of $(T_c - T)/T$ and $(P + P_0)$ between $\ln \eta$ and $\ln V$.

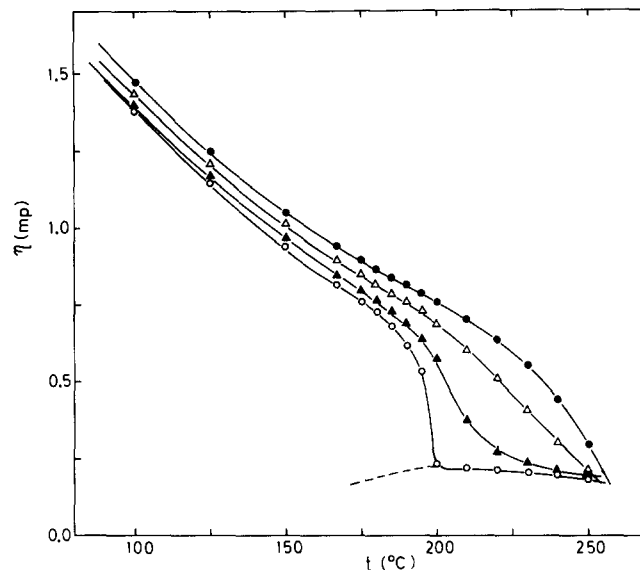


Figure 9 η (millipoise) vs. temperature ($^{\circ}\text{C}$) plot for n-pentane at various pressures (kgf/cm²). (\circ), 35.15 kgf/cm²; (\blacktriangle), 42.18; (\triangle), 56.25; (\bullet), 70.31. The dotted line corresponds to η for gas

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