

The Temperature Dependence of the Doolittle Equation Parameter for Polymer Liquids

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SYNOPSIS

The Doolittle equation parameter for polymer liquids is a function of temperature. Its dependence on temperature can be expressed by a quadratic equation. The constants in the equation are determined for four vinyl-type polymer liquids: polystyrene (PS), poly(vinyl acetate) (PVAc), polydimethylsiloxane (PDMS), and polyisobutylene (PIB). It was found that the Doolittle parameter decreases with increasing temperature. Equations are presented for the pressure and temperature coefficients of viscosity, isoviscous temperature coefficient of volume, and the constant K_m in the Miller equation. Comparisons of the predictions of the equations, with those in the literature, are favorable. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The most commonly used expression, relating viscosity to pressure, is the Doolittle equation¹

$$\ln \eta = \ln A + B_D V_{00} / (V - V_{00}) \quad (1)$$

where V is the specific volume of the liquid polymer at pressure P and temperature T , V_{00} is the occupied volume at zero Kelvin, and A and B_D are parameters. According to Dymond et al.,²⁻⁴ B_D is temperature dependent.

Another equation, which is sometimes useful in correlating viscosity–pressure data, is the Vogel equation⁵

$$\ln \eta = \ln A' + B_V / (T - T_0) \quad (2)$$

where A' , B_V , and T_0 are parameters. Both B_V and T_0 are dependent on pressure. Many years ago, Miller^{6,7} derived the pressure dependence of the parameters, T_0 and B_V , for vinyl-type polymers.

In this article, we derive the temperature dependence of B_D for four polymers: PS, PVAc, PDMS, and PIB. The necessary PVT data are obtained us-

ing the equation of state, proposed by Cho, which takes the form⁸⁻¹⁰

$$V = V_0 [K / (K + P)]^C \quad (3)$$

where V_0 is the zero-pressure volume at T and C is a constant, independent of P and T . The parameter K is independent of pressure and varies with temperature as:

$$K = k_0 \exp(-k_T) \quad (4)$$

$$k_T = k_1 T + k_2 T^2 \quad (5)$$

where k_0 , k_1 , and k_2 are constants for a given polymer liquid. The temperature dependence of V_0 can be expressed by¹⁰

$$\ln V_0 = a_0 + a_1 T + a_2 T^2 \quad (6)$$

where a_0 , a_1 , and a_2 are constants. The parameters in eqs. (3) and (6), for nine liquid polymers, were given in Ref. 10. Volumes, calculated with eqs. (3) and (6), agree with measured values within the accuracy of the measurements, typically 0.001 cm³/g.

RESULTS AND DISCUSSION

Assuming that the temperature dependence of B_D is given by a quadratic equation

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Table I Parameters in Eqs. (3) and (6)^a

	PS	PVAc	PDMS	PIB
a_0	-2.12779×10^{-1}	-3.84716×10^{-1}	-2.25710×10^{-1}	-7.09048×10^{-2}
a_1	5.06870×10^{-4}	6.91153×10^{-4}	8.14263×10^{-4}	5.02334×10^{-4}
a_2	7.30724×10^{-9}	4.32452×10^{-8}	1.53499×10^{-7}	8.75706×10^{-8}
a_3	0	0	0	2.70508×10^{-12}
C	9.8700×10^{-2}	1.07865×10^{-1}	1.17605×10^{-1}	9.77632×10^{-2}
k_0	4.22110×10^3	1.16462×10^4	5.72070×10^3	6.22290×10^3
k_1	1.46813×10^{-3}	6.69306×10^{-3}	5.51024×10^{-3}	3.76464×10^{-3}
k_2	2.45360×10^{-6}	-3.82379×10^{-6}	5.46996×10^{-7}	5.43947×10^{-7}

^a Volumes in cm³/g, pressures in bars, temperatures in K.

$$B_D = b_0 + b_1T + b_2T^2 \quad (7)$$

where b_0 , b_1 , and b_2 are constants, then, from eqs. (1) and (2), we have

$$\begin{aligned} \ln(\eta/\eta_0) &= B_V(P)/[T - T_0(P)] \\ &\quad - B_V(0)/[T - T_0(0)] \quad (8) \\ &= (b_0 + b_1T + b_2T^2) \\ &\quad \times V_{00}[1/(V - V_{00}) - 1/(V_0 - V_{00})] \quad (9) \end{aligned}$$

where η_0 , $B_V(0)$, and $T_0(0)$ are the values at $P = 1$ bar. For four vinyl-type polymers, we fitted the Vogel term data to eq. (9) in order to determine the parameters in eq. (7). The Vogel term data were calculated using $B_V - P$ and $T_0 - P$ data, reported by Miller.^{6,7} In calculating the Doolittle term, the necessary PVT data were calculated from eqs. (3) and (6), with the constants listed in Table I, and the values of V_{00} were calculated from eq. (6) with $T = 0K$. The temperature and pressure range of the data, used for PVT data reduction, were presented in Ref. 10. The results are presented in Table II. Throughout this work, units are cm³/g, bars, and kelvin.

In Table III, the values of $\ln(\eta/\eta_0)$, calculated using eq. (9) for four vinyl-type polymers at various pressures, are compared with those calculated by eq. (8), with $B_V - P$ and $T_0 - P$ data reported by Miller.^{6,7}

Table II Parameters in Eq. (7)

	b_0	$-b_1$	b_2
PS	29.62905	9.61065×10^{-2}	8.12470×10^{-5}
PVAc	35.53602	0.12813	1.24471×10^{-4}
PDMS	2.25740	6.99554×10^{-3}	6.55027×10^{-6}
PIB	4.31827	1.46202×10^{-2}	1.56741×10^{-5}

From eqs. (3) and (6), the compressibility $\beta = (\partial \ln V/\partial P)_T$, and thermal expansivity $\alpha = (\partial \ln V/\partial T)_P$, are expressed as

$$\beta = C/(K + P) \quad (10)$$

and

$$\alpha = \alpha_0 - \beta P(dk_T/dT) \quad (11)$$

where α_0 is the value of α at $P = 1$ bar. The values of α_0 , α , and β are calculated using eqs. (6), (11), and (10), with the constants listed in Table I.

Using eq. (1), we have

$$N_P = (\partial \ln \eta/\partial P)_T = B_D V V_{00} \beta / (V - V_{00})^2 \quad (12)$$

and

$$\begin{aligned} N_T &= (\partial \ln \eta/\partial T)_P \\ &= \frac{V_{00}}{(V - V_{00})} \frac{dB_D}{dT} - B_D V V_{00} \alpha / (V - V_{00})^2 \quad (13) \end{aligned}$$

These can be used to estimate the pressure and temperature coefficients of viscosity, N_P and N_T . From eq. (2), we have¹¹

$$N_T = (\partial \ln \eta/\partial T)_P = -B_D/(T - T_0)^2 \quad (14)$$

which shows that the absolute value of N_T decreases with increasing temperature.

Penwell and Porter ($P. - P.$)^{12,13} determined the pressure dependence of viscosity for polymers using the equivalent expression of the WLF equation, derived from free volume theory.

In Table IV, the calculated values of N_P , N_T , and dV_0/dP , for PDMS at 1 bar and 40°C, are compared with those in the literature. The agreement is good. Using eq. (12), for PS at 1 bar and 190°C, we find $-N_T = 0.102 K^{-1}$, which is in good agreement with

Table III Calculated Values of $\ln(\eta/\eta_0)$ at Various Pressures^a

<i>P</i> (bars)	PS (180°C)		PVAc (110°C)		PDMS (40°C)		PIB (10°C)	
	Calc A	Calc B	Calc A	Calc B	Calc A	Calc B	Calc A	Calc B
200	0.76856	0.76534	0.86619	0.85430	0.23340	0.23256	0.62294	0.66312
400	1.52814	1.53898	1.71678	1.71197	0.46486	0.46848	1.26822	1.32597
600	2.28470	2.30920	2.55693	2.56976	0.69731	0.70352	1.93954	1.99421
800	3.04285	3.09219	3.39069	3.42851	0.93295	0.93724	2.64068	2.65626
1000	3.80635	3.86856	4.22130	4.29176	1.17359	1.17527	3.37566	3.32943

^a The temperatures for calculation are listed in parentheses. Calc A: calculated using eq. (9) with the constants listed in Table II; calc B: calculated using eq. (8) with the B_P - P and T_0 - P data reported by Miller.^{6,7}

experimental value 0.103 K^{-1} , found by Cogswell and McGowan.¹⁴

The calculated values of N_P at various temperatures, in Table V, for PS¹³ of $T_g = 89^\circ\text{C}$ and PVAc¹⁵ of $T_g = 31^\circ\text{C}$, are compared with those in the literature. From the result of the comparison, one sees that the predicted values, using eq. (12), are in reasonable agreement with the experimental data. As pointed out by Goldblatt and Porter,¹³ at low temperatures, Miller's equation tends to predict values somewhat higher than those in the experiments.

According to Miller,¹¹ the special combination of volume-temperature derivatives,

$$K_m = [(\partial V/\partial T)_\eta - (\partial V/\partial T)_P] \quad (15)$$

$$= (\partial V/\partial P)_T / (\partial T/\partial P)_\eta \quad (16)$$

is independent of temperature at atmospheric pressure. This can be rewritten in the form

$$-K_m = N_T(\partial V/\partial P)_T / N_P \quad (17)$$

Using eqs. (12) and (13), this becomes

$$K_m = (V - V_{00})(d \ln B_D/dT) - (\partial V/\partial T)_P \quad (18)$$

At atmospheric pressure, this becomes

$$K_m^0 = (V_0 - V_{00})(d \ln B_D/dT) - (dV_0/dT) \quad (19)$$

A comparison of eq. (18) with eq. (15) shows that

$$(\partial V/\partial T)_\eta = (V - V_{00})(d \ln B_D/dT) \quad (20)$$

For all polymer liquids studied, we found that $dB_D/dT < 0$. Thus, $(\partial V/\partial T)_\eta$ is negative.

Using eqs. (12) and (13), we have

$$-(\partial T/\partial P)_\eta = N_P/N_T = \left[\frac{V - V_{00}}{V\beta} \frac{d \ln B_D}{dT} - \alpha/\beta \right]^{-1} \quad (21)$$

For PS at 1 bar and 190°C , we find $-N_P/N_T = 0.0349 \text{ deg/bar}$, which is in excellent agreement with the literature value¹⁴ of 0.034 deg/bar .

If it is assumed that B_D is independent of temperature, then from eq. (21), we obtain the well-known expression¹⁷

$$N_P/N_T \approx -\beta/\alpha \quad (22)$$

Table IV Predictions of N_P , N_T , dV_0/dT , and K_m^0 for PDMS at 1 bar and 40°C

	$10^3 N_P$ (bar ⁻¹)	$-10^2 N_T$ (deg ⁻¹)	$-10^4 dV_0/dP$	$-10^4 K_m^0$
PDMS ^a	1.295 ^c	1.798 ^d	1.291 ^c	17.9 ^d
	0.73 ^e	1.8 ^e		
PDMS ^b	1.177 ^f	1.813 ^g	1.218 ^h	18.76 ⁱ

^a $M = 30,500$.

^b $M = 47,200$.

^c E. Kuss and M. Taslimi, *Chem.-Ing.-Tech.*, **42**, 1073 (1970).

^d Reference 11, Table I.

^e W. Holzmüller and R. Dinter, *Exp. Techn. Physik*, **8**, 118 (1960).

^f Equation (12).

^g Equation (13).

^h Equation (10).

ⁱ Equation (17).

Table V Predicted Pressure Coefficients for PS and PVAc at Various Temperatures $N_P \times 10^3$ (bars⁻¹)

PS				PVAc			
t °C	P - P . ^a	Miller ^a	This Work ^e	Experimental	t °C	Miller ^b	This Work ^e
150	4.698	6.597	5.069	4.2 ^a	60	8.81	6.763
165			4.429	4.3 ^c	80	6.27	5.676
170	3.267	5.071	4.235	3.9 ^a	100	4.81	4.769
190	2.402	4.10	3.544	3.9 ^a	120	3.88	4.019
				3.5 ^d			

^a Reference 13.^b Reference 15.^c K. H. Hellwege, W. Knappe, P. Paul, and V. Semjonow, *Rheol. Acta*, **6**, 165 (1967).^d F. N. Cogswell and J. C. McGowan, *Brit. Polym. J.*, **4**, 183 (1972).^e Calculated from eq. (12).

Using the concept that the glass transition temperature, T_g , is an isoviscous or isomobility state, we have from eq. (20)

$$(\partial V/\partial T)_n = dV_g/dT \quad (23)$$

$$= (V_g - V_{00})(d \ln B_D/dT) \quad (24)$$

Using this information in eq. (15), the value of K_m° at T_g can be predicted. From the values of V_0 and $d \ln B_D/dT$ for PVAc at $T_g = 31^\circ\text{C}$, we find $10.55 \text{ cm}^3/(\text{g deg})$ for $-10^4 dV_g/dT$ to be in good agreement with the experimental value of $10.8 \text{ cm}^3/(\text{g deg})$, obtained by Miller,¹¹ using the PVT data of McKinney and Goldstein.¹⁶ From this and $10^4 dV_0/dT = 7.1746 \text{ cm}^3/(\text{g deg})$ at T_g , we find $-10^4 K_m^\circ = 17.72 \text{ cm}^3/(\text{g deg})$. This value is close to that found by Miller,¹¹ namely, $17.9 \text{ cm}^3/(\text{g deg})$. Similarly, we find 11.138 and 4.9789 , respectively, leading to $-10^4 K_m^\circ = 16.12 \text{ cm}^3/(\text{g deg})$ for PS at $T_g = 89^\circ\text{C}$. This is also in good agreement with Miller's value¹¹ for the same material, which is $16.9 \text{ cm}^3/(\text{g deg})$.

For PS at 1 bar and 190°C , we find from eq. (10) $10^5 dV_0/dP = -7.9983 \text{ cm}^3/(\text{g bar})$. Using this and experimental values,¹⁴ $N_T = -0.103 \text{ deg}^{-1}$ and $10^3 N_P = 3.5 \text{ bar}^{-1}$, we find from eq. (17) $-10^4 K_m^\circ = 23.538 \text{ cm}^3/(\text{g deg})$. From this result, one sees that K_m° increases with increasing temperature.

CONCLUSIONS

The Doolittle constant can be expressed by a quadratic equation in temperature, which decreases with increasing temperature. Based on this result, the following conclusions are reached: (a) The pressure

coefficient, N_P , decreases with increasing temperature, (b) the temperature coefficient, N_T , is negative and its absolute value decreases with increasing temperature, and (c) the constant K_m° , in Miller's equation, may change with temperature.

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