Mobilities of polymer liquids at constant temperature and at constant volume

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Previously developed relationships between isomobility states and equilibrium $p-v-T$ properties of vinyl polymers are extended to predict mobilities, μ, at constant temperature and at constant volume, with poly(vinyl acetate) as an example. At constant volume, μ changes by several orders of magnitude while the 'internal pressure' remains constant, suggesting that kinetic energy (temperature) dominates in governing μ. From μ at constant temperature the Vogel parameters, B and T_0, are found to increase with pressure, the former increasing linearly. A new Vogel type equation is developed in which one of the parameters, B_v, depends only on the chemical composition of the polymer. Both μ and its 'activation energy' at constant pressure, E_p, are shown to be constant at the glass transition.

INTRODUCTION

It was shown some time ago that for polymer liquids at atmospheric pressure the temperature dependence of Newtonian viscosity and of the α process in dielectric relaxation can be expressed by the Vogel equation with the same B, T_0 constants applying for the two processes[1]. In this work we shall use the term *mobility* μ to encompass both processes and to include the respective temperature and pressure independent pre-exponential terms. Thus, $\mu = \eta_0/\eta = f_{max}/f_0 = \tau_0/\tau$, where η is the Newtonian viscosity, $f_{\max}$ is the frequency at which the dielectric loss factor is at a maximum, and τ is a characteristic relaxation time. Accordingly, the Vogel equation is expressed as:

$$-\ln\mu = B/(T - T_0) \tag{1}$$

Although this equation has ordinarily been used only at atmospheric pressure it will be shown here that it applies at higher constant pressures as well, with the appropriate adjustments of the B and T_0 parameters.

In previous papers[2,3] we reported a new, exact relationship between μ and the equilibrium $p-v-T$ properties of the polymer liquid:

$$-K = (\partial\ln\mu/\partial T)_p(\partial v/\partial p)_T/(\partial\ln\mu/\partial p)_T \tag{2}$$

where

$$K = (\partial v/\partial T)_\mu - (\partial v/\partial T)_p \tag{2a}$$

While equation (2) is thermodynamically exact, applying to any $p-v-T$ state for any liquid down to the glass transition, two unexpected features were discovered empirically for vinyl type polymers: (a) for a given polymer liquid at atmospheric pressure K is insensitive to temperature; (b) it has the same value, $-10^4K = 17 \pm 1$ cm^3/g°C, for different vinyl polymers. For Newtonian viscosity this value of K applies only up to M_c, the 'critical entanglement' molecular weight, but dielectric relaxation data also give the same value for much higher molecular weights[3]. This implies that the same *local* motion of the polymer segments is involved in viscous flow as occurs in dipole orientation (α process) and is consistent with the observation that the same Vogel constants, B and T_0, apply for the two processes.

A preliminary report[4], with the viscosity of polystyrene as an example, outlined procedures by which equations (1) and (2) could be used to estimate mobilities at constant temperature and at constant volume. The former is the pressure coefficient, $(\partial\ln\mu/\partial p)_T$, which has been measured directly for a number of polymers by viscosity and/or by dielectric relaxation. However, no direct measurements at constant volume have been reported.

The average molecular separation and hence the intermolecular potential energy remain constant at constant volume, leaving kinetic energy (temperature) as the primary variable. In principle this separation of the volume and temperature variables should make polymer liquid relaxation processes more amenable to theoretical interpretation at a molecular level.

GENERAL EQUATIONS

The procedure for estimating isothermal and isochoric mobilities is to project parallel isomobility lines onto the P_0 (atmospheric pressure) isobar where μ can be calculated by equation (1).

In *Figure 1a*, for constant temperature, v_1, v_2, v_3, etc., are the volumes on the T_1 isotherm for pressures P_0, P_1, P_2, etc. Let $\Delta v = v_1 - v_2$, $v_1 - v_3$, etc., and $\Delta T = T_1 - T_2$, $T_1 - T_3$, etc. on the P_0 isobar and then it can be shown from the geometry that:

$$\Delta T = -\Delta v/K \tag{3}$$

The mobilities at T_1, T_2, etc., corresponding to the mobilities at v_1, v_2, etc. on the T_1 isotherm are then calculated by equation (1). This process is repeated for other isotherms.

For constant volume (*Figure 1b*), T_v, T_v', etc., are temperatures on the indicated isochor for pressures P_1, P_2, etc.

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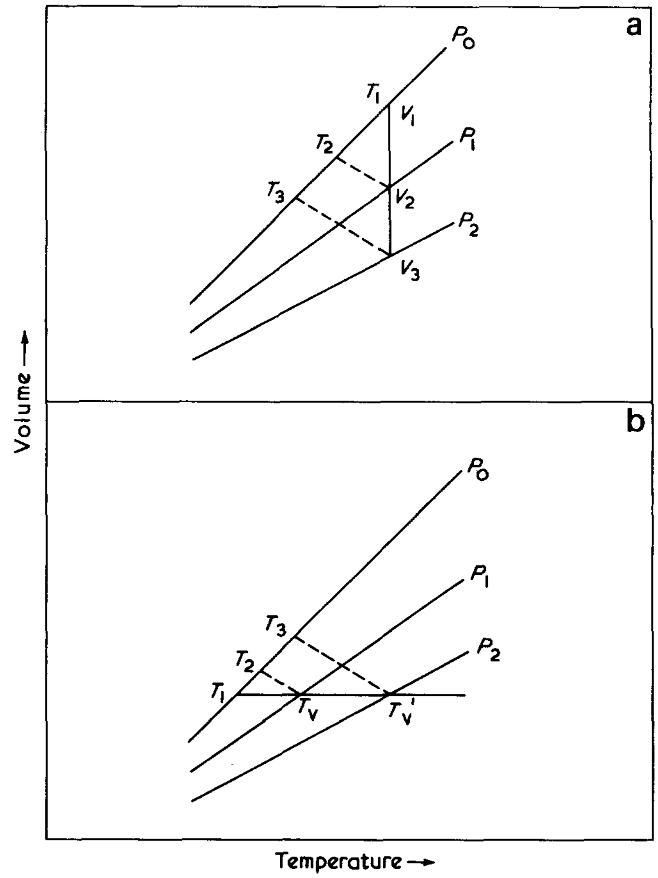

Figure 1 Generalized p–v–T diagrams. (a) Isothermal mobilities. (b) Isochoric mobilitis. — — —, Parallel isomobility lines

Let $\Delta T_v = T_1 - T_v$, $T_1 - T_v'$, etc., and $\Delta T = T_1 - T_2$, $T_1 - T_3$, etc., then it can be shown from the geometry that:

$$\Delta T = [(\partial v/\partial T)_\mu / K]\Delta T_v \qquad (4)$$

from which the series of temperatures T_1, T_2 etc., at P_0, give, using equation (1), the mobilities at constant volume for temperatures T_1, T_v, T_v', etc. This process is then repeated for other isochors.

It is of interest also to estimate the temperature coefficient of mobility at constant volume. The temperature coefficient at constant pressure along the P_0 isobar is found by differentiating equation (1):

$$(\partial \ln\mu/\partial T)_P = B/(T - T_0)^2 \qquad (5)$$

By equation (4), which relates increments in T and T_v, we then obtain for constant volume:

$$(\partial \ln\mu/\partial T)_v = [(\partial v/\partial T)_\mu/K]\, B/(T - T_0)^2 \qquad (6)$$

The 'activation energy' at constant volume is:

$$E_v = RT_v^2(\partial \ln\mu/\partial T)_v \qquad (7)$$

RESULTS

Equations (1)–(7) were applied to high molecular weight poly(vinyl acetate) (PVAc) for which detailed p–v–T data are available in the paper of McKinney and Goldstein[5] and for which dielectric relaxation has been measured over broad ranges of temperature and pressure by O'Reilly[6]. Compressibilities were calculated using the Tait equation with the constants reported by Beret and Prausnitz[7] applying up to 1000 bar pressure in the temperature range 64°–120°C:

$$(\partial v/\partial p)_T = -cv_0/(p + b) \qquad (8)$$

The volumes v_0 at P_0 were taken from *Table 1* of ref 5, as was the value $10^4(\partial v/\partial T)_p = 6.25$ cm^3/g°C. The Vogel constants at P_0 derived from viscosity measurements[8], $B = 2183$°C and $T_0 = -25$°C, give excellent agreement with the P_0 curve in *Figure 6* of the O'Reilly paper[6].

Isothermal mobilities

The pressure coefficients of mobility at P_0 were calculated from equations (2) and (5) with $-10^4K = 17.0$ cm^3/g°C. These are listed in *Table 1* and plotted in *Figure 2*, together with the experimental values of O'Reilly[6]. The latter show a somewhat less regular behaviour with temperature.

The isothermal mobilities at higher pressures were calculated as described in *Figure 1a* for 200 bar increments up to 800 bar. The Δv values (equation 3) were derived directly from *Table 1* of ref 5. *Table 2* and *Figure 3* show the results. It may be seen that $-\ln\mu$ is linear in pressure, consistent with experiment data[6], and the slopes are in agreement with the pressure coefficients listed in *Table 1.*

Table 1 Pressure coefficients of mobility[a]

T(°C)	v_0 (cm^3/g)	$-10^5(\partial v/\partial p)^b$ (cm^3/g bar)	$-10^3(\partial \ln\mu/\partial p)_T$ (bar^{-1})
60	0.861	4.96	8.81
80	0.873	5.39	6.27
100	0.886	5.85	4.81
120	0.8985[c]	6.36	3.88

[a] At P_0 given by equations (2) and (5); [b] Using equation (8); c = 0.1046[7], b = 1817, 1695, 1583, 1478 bars, respectively[7];
[c] by linear extrapolation

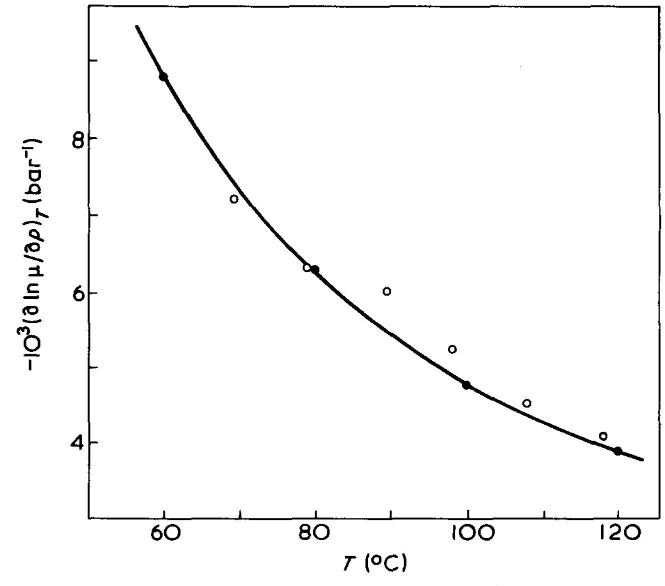

Figure 2 Pressure coefficients of mobility at P_0: ●, from equations (2) and (5); ○, results of O'Reilly[6]

Table 2 Isothermal mobilities

P (bar)	*T* (°C)	$-\ln\mu$	*T* (°C)	$-\ln\mu$	*T* (°C)	$-\ln\mu$
0	60[a]	25.7	80[a]	20.8	100[a]	17.5
200	54.5	27.4	74.1	22.0	93.4	18.4
400	49.8	29.2	68.9	23.2	87.7	19.4
600	45.3	31.0	64.1	24.5	82.7	20.3
800	41.2	33.0	59.7	25.8	78.1	21.2

[a] Temperature of the isotherm in *Figure 1a*. Remaining temperatures in each column were calculated by equation (3)

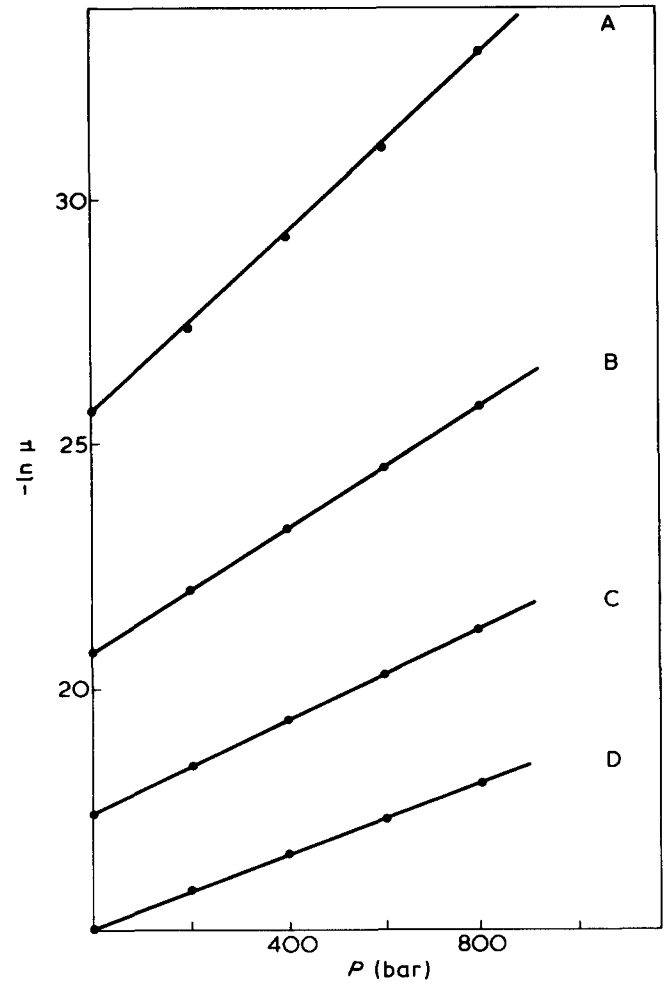

Figure 3 Isothermal mobilities as functions of pressure: A, 60°; B, 80°; C, 100°; D, 120°C

Isochoric mobilities

Mobilities were calculated at three constant volumes as shown in *Figure 1b*. In *Table 3*, T_v is the temperature at which the isochor intersects each indicated isobar and was obtained from a large scale plot of the $p-v-T$ data in *Table 1* of ref 5 (see, for example, *Figure 4* of ref 5). The corresponding isomobility temperature T on the P_0 isobar was derived by equation (4) with $-10^4K = 17$ and $-10^4(\partial v/\partial T)_\mu = 10.75$ cm^3/g°C. The mobilities were then calculated at temperatures T using equation (1). The 'activation energies' at constant volume, E_v, given by equations (6) and (7) are also listed in *Table 3*.

The thermal pressure coefficients, $(\partial p/\partial T)_v$, found by plotting P against T_v in *Table 3*, are constant at constant volume. From these, the 'internal pressure', $(\partial E/\partial v)_T$, was derived as indicated in *Table 4*. For each constant volume there is a barely perceptible variation in the 'internal pressure' suggesting that the intermolecular cohesive energy remains essentially constant, while the mobility changes by several orders of magnitude (*Figure 4*). Thus we conclude that the mobility is dominated by the kinetic energy (temperature).

Pressure dependence of Vogel parameters B *and* T_0

The isothermal change in mobility with pressure is given by:

$$\Delta\ln\mu = (\partial\ln\mu/\partial p)_T\Delta P \tag{9}$$

recalling that the pressure coefficient is independent of pressure (*Figure 3*). In terms of the Vogel equation:

$$-\Delta\ln\mu = B'/(T - T_0') - B/(T - T_0)$$

where B', T_0' are the values at pressure P, while B, T_0 apply at P_0. Rearranging, we obtain:

$$[B/(T - T_0) - \Delta\ln\mu]^{-1} = T/B' - T_0'/B' \tag{10}$$

Hence a plot of the left-hand term against T will be linear with a slope of $1/B'$ and an intercept of $-T_0'/B'$. With the

Table 3 Mobilities at constant volume

P (bar)	T_v (°C)	*T* (°C)	$-\ln\mu$	E_v (kcal/mol)
v = 0.850 cm^3/g				
0	42.5	42.5	32.3	59.9
200	57.0	51.7	28.5	50.8
400	71.5	60.8	25.4	44.2
600	87.5	71.0	22.7	38.7
800	102.0	80.1	20.8	34.9
v = 0.860 cm^3/g				
0	58.5	58.5	26.1	43.2
200	74.5	68.6	23.3	37.8
400	90.0	78.4	21.1	33.8
600	107.0	89.2	19.1	30.4
v = 0.870 cm^3/g				
0	74.5	74.5	21.9	33.5
200	91.5	85.2	19.8	30.0
400	108.5	96.0	18.0	27.3

Table 4 Internal pressures[a] at constant volume

P (bar)	$(\partial E/\partial v)_T$ (cal/cm^3)		
0	101.4	100.0	99.7
200	101.3	100.1	99.8
400	101.2	100.0	99.9
600	101.5	100.3	–
800	101.4	–	–
	v (cm^3/g)		
	0.850	0.860	0.870
	$(\partial p/\partial T)_v$(bar/°C)		
	13.44	12.62	12.00

[a] $(\partial E/\partial v)_T = T(\partial p/\partial T)_v - P$

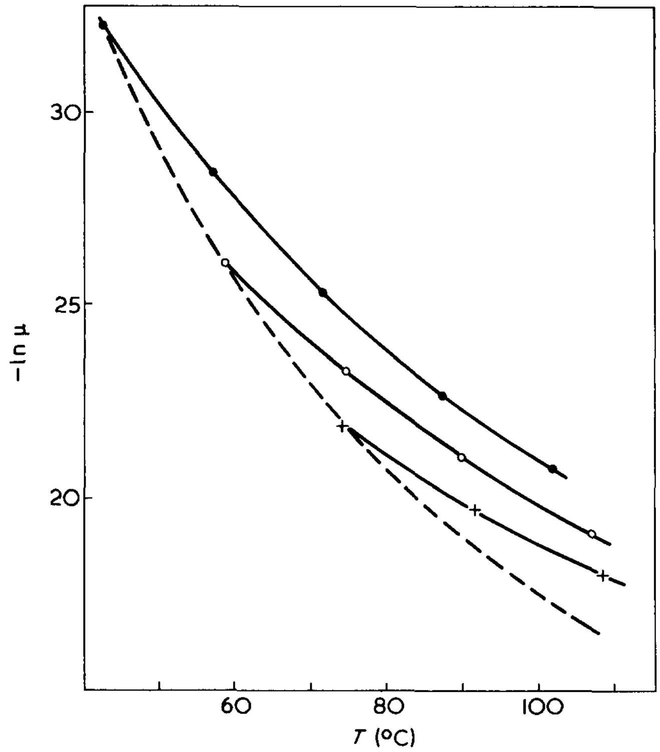

Figure 4 Isochoric mobilities as functions of temperature: ●, 0.850 cm^3/g; ○, 0.860 cm^3/g; +, 0.870 cm^3/g; — — — —, mobilities on P_0 isobar

pressure coefficients from *Table 1*, these plots are displayed in *Figure 5* and the final results listed in *Table 5*. B' turns out to be linear in pressure and $dB/dP = 0.336°C/bar$, while T_0' shows a curvature with an intial slope (P_0) of ~0.016°C/bar (*Figure 6*).

The Vogel equation:

$$-\ln\mu = B'/(T - T_0') \tag{11}$$

with B' and T_0' from *Table 5* or interpolated from *Figure 6* may now be used to calculate the mobility at any pressure up to 1000 bar.

Isomobility states

By imposing parallel isomobility lines on a series of V–T isobars (see *Figures 1a* and *1b*) isomobility temperatures T_μ may be derived for each pressure. This was done for PVAc for initial (P_0) temperatures of 80°, 60° and 31.5°C (T_g), with $-10^4(\partial v/\partial T)_\mu = 10.75$. *Table 6* lists the T_μ and T_g values, the latter taken directly from *Table 9a* of ref 5. It is seen that the mobilities at the glass transition, T_g, calculated by equation (11), are quite constant, as are the 'activation energies' at constant pressure given by the equation:

$$E_p = RB'[T_g/(T_g - T_0')]^2 \tag{11a}$$

Similarly, $\ln\mu$ and E_p calculated at the T_μ and T_μ' temperatures in *Table 6* are found to be constant.

Some years ago and in another context Fox and Flory[9] showed from viscosity measurements on polystyrene that E_p at T_g was essentially constant, but apparently they did not treat the glass transition as an isomobility state.

Mobility as a cooperative process

Following Adam and Gibbs[10] we consider polymer liquid mobility as a cooperative kinetic process and obtain at *constant pressure:*

$$-\ln\mu = Z_pE_0/RT \tag{12a}$$

$$= E_p/Z_pRT \tag{12b}$$

$$Z_p = T/(T - T_0') \tag{12c}$$

Z_p is the number of main chain segments in the cooperative unit which must simultaneously overcome the individual barriers (E_0) to their rearrangement. With equation (12c) defining Z_p and with $E_0 = RB'$, equations (12a) and (12b) become identical to the Vogel equation (11).

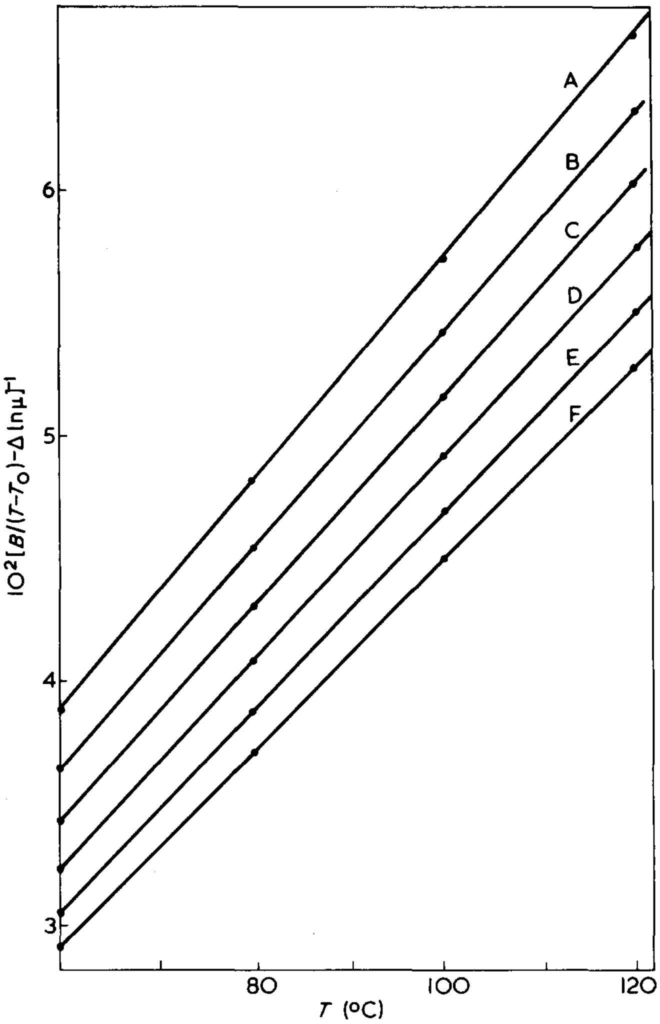

Figure 5 Evaluation of pressure dependence of Vogel parameters using equation (10). Isobars: A, 0; B, 200; C, 400; D, 600; E, 800; F, 1000 bar

Table 5 Pressure dependence of Vogel parameters

P(bar)	T_0' (°C)	B' (°C)
0	−25.00	2183
200	−21.85	2246
400	−19.16	2311
600	−16.90	2380
800	−14.80	2448
1000	−13.00	2519

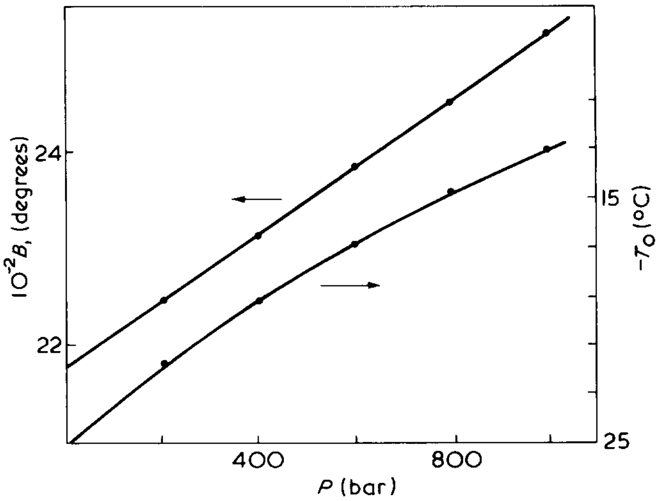

Figure 6 Vogel parameters as functions of pressure

Table 6 Isomobility states

P (bar)	T_μ (°C)	T'_μ (°C)	T_g (°C)	$-\ln\mu^a$	E_p^b (kcal/mol)
0	80.0	60.0	31.50	38.6	128.2
200	86.0	65.5	36.53	38.5	128.7
400	91.5	70.7	41.05	38.4	128.5
600	97.0	75.7	45.08	38.4	128.1
800	102.0	80.5	48.46	38.7	127.4

[a] At T_g, $-\ln\mu = B'/(T_g - T_0')$; [b] at T_g by equation (11a)

It may be noted in passing that using equation (12c), Z_p increases as the liquid volume decreases, i.e. the smaller the unoccupied volume the larger is the cooperative unit, which seems reasonable.

Analogous equations may be considered for *constant volume:*

$$-\ln\mu = E_v/Z_vRT \tag{13a}$$

$$= B_v/(T - T_{0v}) \tag{13b}$$

$$Z_v = T/(T - T_{0v}) \tag{13c}$$

With the $\ln\mu$ and E_v data from *Table 3*, Z_v was calculated by equation (13a), then T_{0v} by equation (13c), and finally B_v by equation (13b). It was found that T_{0v} was independent of pressure, depending only on the volume, while most significantly, B_v was independent of both pressure and volume.

Calculations were then made only at atmospheric pressure (P_0) over a wider range of volumes than in *Table 3*. For the special case of the P_0 isobar it can be shown that:

$$E_v/E_p = Z_v/Z_p = (T - T_0)/(T - T_{0_v}) = B/B_v$$

$$= (\partial v/\partial T)_\mu/K \tag{14}$$

For PVAc, the last term in equation (14) is $-10.75 \times 10^{-4}/-17 \times 10^{-4} = 0.632$. The results are listed in *Table 7*. As mentioned earlier, T_{0v} is a unique function of v and, as seen in *Figure 7*, the relationship is linear. It should be noted that linear extrapolations of $v - T_{0v}$ and v–T (P_0) intersect at −25°C, the T_0 of the simple Vogel equation at P_0. Also, the slope of the v–T_{0v} line is identical to the value of $(\partial v/\partial T)_\mu$. Thus:

$$T_{0v} = T_0 + (v - v_0)/(\partial v/\partial T)_\mu \tag{15}$$

in which for PVAc, $T_0 = -25$°C, $v_0 = 0.808$ cm^3/g and $-10^4(\partial v/\partial T)_\mu = 10.75$ cm^3/g°C. It is emphasized that while equations (13b) and (15) were derived via constant volume considerations, they do in fact describe $\ln\mu$ at any specified liquid volume regardless of the temperature or pressure.

Finally, if equation (13b) is converted into a 'free-volume' form:

$$-\ln\mu = B_v'/(v - v_0) \tag{16}$$

with $v_0 = 0.808$ cm^3/g (a constant), B_v' is not independent of pressure but decreases uniformly from a value of 1.36 (temperature independent) at P_0 to 0.62 at 800 bar. This, of course, is consistent with the observation that $-\ln\mu$ decreases with increasing temperature at constant volume (*Figure 4*) or, conversely, that the liquid volume decreases with increasing temperature at constant μ.

Table 7 Evaluation of equation (13b)^a

v (cm^3/g^b)	T(°C^b)	T_{0v}(°C)
0.8436	31.5 (T_g)	−57.85
0.850	42.5	−64.2
0.860	58.5	−73.4
0.870	74.5	−82.3
0.880	90.5	−92.2
0.890	106.0	−101.1
0.899	120.0	−109.2

[a] $B_v = 3451$°C throughout; [b] v, T at P_0

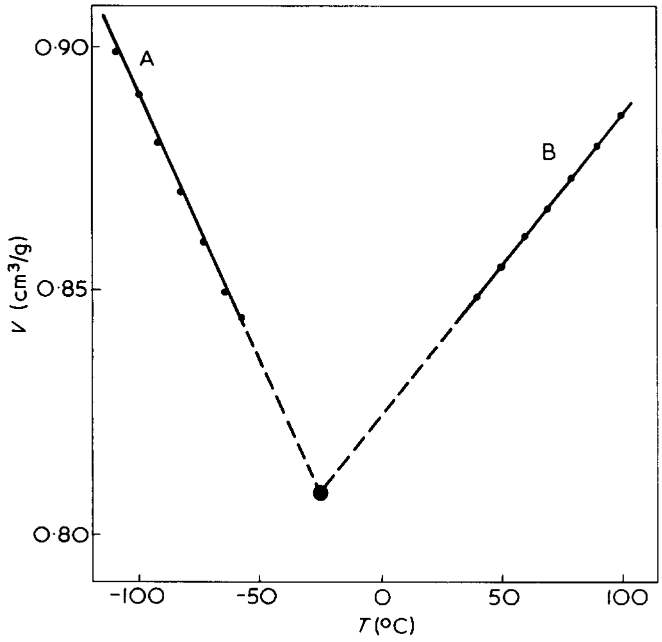

Figure 7 A, T_{0v} (equation 13b) as a function of specific volume; B, temperature *versus* volume on P_0 isobar. ●, $T = -25$°C, $v = 0.808$ cm^3/g

DISCUSSION

Procedures for estimating mobilities of vinyl polymer liquids at constant temperature and at constant volume have been described. For the latter, only the Vogel constants, B and T_0, at atmospheric pressure (P_0) and the v–T isobar at P_0 are needed. The estimates for constant temperature require, in addition, equilibrium p–v–T data at higher pressures, either explicit or as expressed by an accurate equation of state such as the Tait equation. We suggest that these estimated mobilities should be sufficiently accurate to assess the gross features of relaxation theories for these polymer liquids.

The simple Vogel equation (1) has been extended to include the effect of pressure (equation 11). It has been advanced further to equation (13b), whose T_{0v} parameter can be directly related to T_0 in the simple Vogel equation by equation (15), and most importantly, whose B_v parameter depends only upon the chemical composition of the polymer. It should be noted that all of the ratios designated in equation (14) will generally apply at P_0 for vinyl polymers but with some variation in their actual values due to differences in $(\partial v/\partial T)_p$ and hence $(\partial v/\partial T)_\mu$ with K constant (see equation 2a).

This work confirms the glass transition as an isomobility state with respect to *local* motion of polymer segments (i.e. rotation about main chain bonds) which is governed by the Vogel term, $B/(T - T_0)$. The reciprocal at T_g is, of course, the well known WLF value, *approximately* 0.025[11]. Above T_g, different polymers will be in isomobility states at equal values of $B/(T - T_0)$.

The Vogel parameters, B and T_0, are completely independent of each other. On the premise that the predominant local motion involved in polymer liquid mobility is rotation about main chain bonds and following Adam and Gibbs[10] we have suggested that B is simply related to the average intramolecular barrier to such rotation in the 'isolated' chain[12,13]. However, the observed pressure dependence of B implies that such a relationship is more complex.

To be consistent with the experimental Vogel equation, the size of the cooperative unit, Z, which the Adam–Gibbs theory[10] purports to derive, must be as defined by equation (12c), becoming infinite at T_0. This theory has assumed that T_0 is identical to T_2, the temperature at which the *configurational* (i.e. excess) entropy extrapolates to zero[14]. However, we have shown that for some polymers $T_2 \ll T_0$, and have suggested that T_0 is the temperature at which the *conformational* entropy, associated specifically with rotational isomerization about main chain bonds, extrapolates to zero[15,16].

We are continuing this work with vinyl (and other) polymers of widely differing glass transition temperatures with the aim of quantitatively defining the molecular parameters that govern mobilities of polymer liquids.

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