Semiempirical equation of state for polymers and simple liquids under high pressure

S. Saeki, M. Tsubokawa and T. Yamaguchi
Department of Polymer Engineering, Fukui University, Fukui 910, Japan
(Received 15 July 1988; revised 24 August 1988; accepted 1 September 1988)

The semiempirical equation of state for polymers polyethylene (PE), poly(n-butyl methacrylate) (PNBMA) and polystyrene (PS) for pressures up to 2 kbar, five hydrocarbons from n-heptane to n-octadecane over 0 to 1.2–9.0 kbar, five organic liquids, including carbon tetrachloride (CCl_4), over 0 to2.0–12.0 kbar, water up to 10 kbar and argon up to 3 kbar has been derived by using experimental data for specific volume V, compressibility β_T and thermal expansion coefficients α_P under high pressure published by Simha *et al.*, Hellwege *et al.*, Bridgman, Streett and others on the basis of the homogeneous function approach. The equations derived in this work under a constant temperature are:

$$\ln V \sim -(P+P_0)^{1-m_0}$$

$$\beta_T \sim (P+P_0)^{-m_0}$$

$$\alpha_P \sim (P+P_0)^{-n_0}$$

where P_0 is a constant with respect to pressure but depends on temperature, and m_0 and n_0 are constants determined from the experimental data. Values of m_0 range from 0.76 to 0.99, with an average value 0.87 for polymers and simple liquids including water and argon, while values of n_0 for α_P for argon are around 0.50 over 90–150 K.

(Keywords: equation of state; high pressure; polymer; simple liquids; Tait equation)

INTRODUCTION

Pressure is an important variable in the equation of state for liquids as well as temperature. Systematic examination of the function of P, V and T in the equation of state is possible by introducing pressure as a thermodynamic variable at constant temperature. Bridgman, the pioneer in high pressure physics, published useful data for P–V–T behaviour for simple liquids over the pressure range 0–12 kbar[1]. The pressure dependence of molar volume, compressibility β_T and thermal expansion coefficient α_P for argon over several kilobars have been measured by many authors[2–5]. The specific volume of polymers under high pressure over 2 kbar has been determined experimentally by Simha *et al.*[6] and Hellwege *et al.*[7]. The most useful equation of state for polymer liquids is the reduced equation of state derived by Flory *et al.*[8], where the Tonks model and the van der Waals model are used. The Simha and Somcynsky theory is the most powerful for predicting P–V–T behaviour over a wide range of temperature and pressure and its usefulness is proved by extensive data[9–14] where the Tait equation is a basic equation for predicting P–V behaviour in polymer liquids. Dee and Walsh[15,16] have proposed a modified cell model equation of state for polymer liquids and describe the P–V–T data more accurately. Iwai and Arai[17] proposed a semiempirical equation of state for molten polymers and hydrocarbon liquids based on the Flory theory of corresponding states[8]. McGowan[18] discussed the effects of pressure and temperature on the densities of liquid polymers and derived an equation where the parachor and the molecular weight for the repeating unit are introduced.

In a previous work[19] we derived a semiempirical equation of state based on the homogeneous function method and obtained a good prediction of P–V–T behaviour in the non-critical and critical regions in the limited pressure range where pressure is negligible compared to $\gamma_v T$. In this work we try to extend the equation of state over the high pressure range to 12 kbar and examine whether the experimental data on the pressure dependence of the specific volume, compressibility β_T, and thermal expansion coefficient α_P can be predicted or not.

DEVIATION OF EQUATION OF STATE UNDER HIGH PRESSURE

In a previous work[19] we obtained an equation of state based on the homogeneous functions approach. The internal energy $E(V, T)$, the entropy $S(V, T)$ and the equation of state are expressed as follows:

$$E(V,T) = E(T) + a_0(\gamma_v T - P)V\{V/(V_c - V)\}^{b_0} \quad (1)$$

where γ_v is the thermal pressure coefficient

$$S(V,T) = S(T) + \alpha_0 \gamma_v V\{V/(V_c - V)\}^{\beta_0} \quad (2)$$

and

$$P = c_1(X^{\beta_0}/V)\exp(\alpha_0^{-1}I_{\beta_0})T - c_0(X^{b_0}/V)\exp(a_0^{-1}I_{b_0}) \quad (3)$$

Here a_0, b_0, α_0, β_0, c_0 and c_1 are constants and X is defined by

$$X = (V_c - V)/V \quad (4)$$

0032-3861/89/040672-05$03.00

where V_c is the critical volume. The thermal expansion coefficient α_P calculated from equation (3) is given by

$$\begin{aligned}(\alpha_P T)^{-1} = {} & \beta_0\{V_c/(V_c - V)\} + 1 - \alpha_0^{-1} V(\partial I_{\beta_0}/\partial V)_p \\ & - [b_0\{V_c/(V_c - V)\} + 1 \\ & - a_0^{-1} V(\partial I_{b_0}/\partial V)_p](1 - P/\gamma_v T) \qquad (5)\end{aligned}$$

where I_y for $y = \beta_0$ or b_0 is defined by

$$I_y = \int_{V_c}^{V} X^y/V \, dV \qquad (6)$$

In this work we assume that $(P/\gamma_v T) \ll 1$ under high pressure due to an increase of γ_v with pressure, which will be discussed later. Then we obtain the equation for α_P for high pressure (h.p.):

$$(\alpha_P T)^{-1} = X^{\beta_0}(a_0^{-1} - \alpha_0^{-1}) \quad \text{(h.p.)} \qquad (7)$$

which is the same as that at $P \approx 0$[19]. The expression for γ_v is also obtained:

$$\gamma_v = c_1(X^{\beta_0}/V)\exp(\alpha_0^{-1} I_0) \quad \text{(h.p.)} \qquad (8)$$

where I_0 is defined by

$$I_0 = \int_{V_c}^{V} X^{\beta_0}/V \, dV \qquad (9)$$

The compressibility β_T is obtained using the relation $\beta_T = \alpha_P/\gamma_v$:

$$\beta_T = \{c_1(a_0^{-1} - \alpha_0^{-1})\}^{-1}(V/T)X^{-2\beta_0}\exp(-\alpha_0^{-1} I_0) \quad \text{(h.p.)} \qquad (10)$$

The function of P along the isotherm is given using equation (10) by

$$\begin{aligned}& P(V) - P(V_0) \\ & = -c_1(a_0^{-1} - \alpha_0^{-1})T \int_{V_0}^{V} X^{2\beta_0} V^{-2} \exp(\alpha_0^{-1} I_0) \, dV \qquad (11)\end{aligned}$$

where the integration is carried out over V_0 at $P_0 = P(V_0)$ to V at P under a constant temperature. By using the approximation that I_0 in equation (11) is constant over a very small range of V to V_0, where V at 12 kbar is less than V_0 at 1 bar by about 30% or less in most liquids[1], equation (11) is expressed as

$$P(V) - P(V_0) = A_0(T) \int_{X_0}^{X} X^{2\beta_0} \, dX \qquad (12)$$

where

$$A_0(T) = c_1(a_0^{-1} - \alpha_0^{-1})T\{\exp(\alpha_0^{-1} I_0)\} V_c^{-1}$$

is a function of temperature. It is more convenient to rewrite equation (12) as

$$P(V) + P_0(T) = f_0(T) X^{2\beta_0 + 1} \qquad (13)$$

where

$$P_0(T) = A_0(T) X_0^{2\beta_0 + 1}/(2\beta_0 + 1) - P(V_0)$$

and

$$f_0 = A_0(T)/(2\beta_0 + 1) > 0$$

The expression for β_T as a function of pressure is derived using equations (10) and (13) as

$$\beta_T = A(T)\{P + P_0(T)\}^{-2\beta_0/(2\beta_0 + 1)} \qquad (14)$$

where the approximation $V \exp(-\alpha_0^{-1} I_0) = \text{const.}$ over the pressure range investigated is used in equation (10) and therefore $A(T)$ is a complicated function of T determined from equations (10) and (13).

On the other hand α_P as a function of pressure is derived using equations (7) and (13) as

$$\alpha_P = B(T)\{P + P_0(T)\}^{-\beta_0/(2\beta_0 + 1)} \qquad (15)$$

The expression for γ_v is obtained from equations (14) and (15) as

$$\gamma_v = C(T)\{P + P_0(T)\}^{\beta_0/(2\beta_0 + 1)} \qquad (16)$$

where $C(T) = B(T)/A(T)$. From equation (14), a relation between V and P is derived:

$$\ln V/V_0 = -D(T)\{P + P_0(T)\}^{1 - 2\beta_0/(2\beta_0 + 1)} + C_0 \qquad (17)$$

where C_0 is a constant. It is noteworthy that the index in the expression for α_P, $-\beta_0/(2\beta_0 + 1)$, is half that in the expression for β_T, and is opposite in sign to but of the same magnitude as that in the expression for γ_v (see equations (14)–(16)).

Table 1 Comparison between experimental[a] and calculated[b] values of molar volume V, compressibility β_T and thermal expansion coefficient α_P under pressure for argon at 130.0 K

P (bar)	V_{exp} (cm^3 mol^{-1})	V_{cal} (cm^3 mol^{-1})	$10^4\beta_{T,exp}$ (bar^{-1})[c]	$10^4\beta_{T,cal}$ (bar^{-1})	$10^3\alpha_{P,exp}$ (K^{-1})	$10^3\alpha_{P,cal}$ (K^{-1})
40.52	36.60	36.60	10.47	10.47	9.37	9.38
81.04	35.32	35.30	7.47	7.51	7.37	7.37
101.3	34.82	34.79	6.57	6.60	6.74	6.74
202.6	33.04	32.98	4.20	4.19	4.98	4.99
405.2	30.96	30.89	2.52	2.50	3.58	3.60
607.8	29.66	29.58	1.83	1.81	2.94	2.95
810.4	28.69	28.62	1.44	1.43	2.55	2.56
1013.0	27.94	27.86	1.20	1.19	2.28	2.28
1215.6	27.32	27.24	1.03	1.02	2.08	2.08
1418.2	26.80	26.71	0.90	0.90	1.92	1.93
1620.8	26.34	26.25	0.80	0.80	1.79	1.80
1823.4	25.93	25.84	0.72	0.73	1.69	1.69
2026.0	25.58	25.47	0.66	0.66	1.60	1.61

[a] Data are taken from Reference 2

[b] V is calculated from equation (17), β_T from equation (14) and α_P from equation (15)

[c] 1 bar = 10^5 Pa

Table 2 Comparison between experimental[a] and calculated[b] values of specific volume V_{rel} and β_T for *n*-heptane at 120°C

P (bar)	$V_{\mathrm{rel,exp}}$	$V_{\mathrm{rel,cal}}$	$10^4\beta_{T,\mathrm{exp}}$ (bar^{-1})	$10^4\beta_{T,\mathrm{cal}}$ (bar^{-1})
0.980	1.0000	1.0000		3.62
98.0	0.9705	0.9707	2.63	2.63
196.0	0.9483	0.9487	2.08	2.09
294.0	0.9306	0.9312	1.74	1.74
392.0	0.9162	0.9166	1.50	1.50
490.0	0.9033	0.9041	1.32	1.32
588.0	0.8929	0.8930	1.19	1.19
686.0	0.8829	0.8832	1.08	1.08
784.0	0.8743	0.8743	0.99	0.99
882.0	0.8657	0.8662	0.91	0.91
980.0	0.8584	0.8588	0.85	0.85
1078.0	0.8515	0.8519	0.80	0.80
1176.0	0.8448	0.8455	0.75	0.75

[a] Data are taken from Reference 24

[b] V_{rel} is calculated from equation (17), $V_{\mathrm{rel}} = V/V_0$ (1 bar), and β_T from equation (14)

RESULTS

Comparisons between experimental and calculated values of V, β_T and α_P are given for argon and *n*-heptane in *Tables 1* and *2*. Comparisons between the specific volumes of polymers and simple liquids such as isopentane and water are listed in *Tables 3* and *4*, which show good agreement, within <1%, between the observed and calculated values over 12 kbar. The values of $2\beta_0/(2\beta_0+1)=m_0$, $\beta_0/(2\beta_0+1)=n_0$ and P_0 and other values used in this work are listed in *Tables 5* and *6*, where β_0 is also listed. It is interesting to note that values of β_0 obtained from the temperature dependence of α_P in previous work[19] are in the range 2.6–2.8, which can be compared with values of β_0 obtained from the pressure dependence of β_T for argon in *Table 5*. From *Table 5* we obtain $m_0/n_0 \sim 2.0$, which is predicted by equations (14) and (15).

Table 3 Comparison between the experimental[a] and calculated[b] values of specific volume under pressure for polystyrene (PS), polyethylene (PE) and poly(*n*-butyl methacrylate) (PNBMA)

	PS (248.9°C)			PE (hi-M_w) (187.8°C)		PNBMA (82.3°C)	
P (bar)	V_{exp} (cm^3 g^{-1})	V_{cal} (cm^3 g^{-1})	P (bar)	V_{exp} (cm^3 g^{-1})	V_{cal} (cm^3 g^{-1})	V_{exp} (cm^3 g^{-1})	V_{cal} (cm^3 g^{-1})
1.0	1.079	1.079	1	1.3306	1.3304	0.9840	0.9840
196.1	1.061	1.060	100	1.3156	1.3153		
392.3	1.043	1.043	200	1.3022	1.3019	0.9723	0.9727
588.4	1.028	1.029	300	1.2902	1.2899		
784.5	1.015	1.016	400	1.2792	1.2790	0.9627	0.9627
980.7	1.004	1.004	600	1.2603	1.2600	0.9537	0.9538
1176.8	0.9930	0.9932	800	1.2439	1.2437	0.9457	0.9457
1372.9	0.9843	0.9834	1000	1.2294	1.2295	0.9381	0.9383
1569.1	0.9756	0.9743	1200	1.2168	1.2169	0.9310	0.9315
1765.2	0.9671	0.9658	1400	1.2049	1.2056	0.9247	0.9252
1961.3	0.9597	0.9579	1600	1.1941	1.1954	0.9188	0.9193
			1800	1.1845	1.1860	0.9129	0.9138
			2000	1.1759	1.1773	0.9079	0.9086

[a] Data are taken from References 7 and 18 for PS, Reference 11 for PE and Reference 6 for PNBMA

[b] Calculated values are obtained from equation (17)

Table 4 Comparison between experimental[a] and calculated[b] values of specific volume V (cm^3 g^{-1}) under pressure for simple liquids and an oligomer

	Isopentane (50°C)		Water (50°C)		Ethyl alcohol (20°C)		Glycerine (30°C)			9-*n*-octyl heptadecane (135°C)	
P (bar)	V_{exp}	V_{cal}	V_{exp}	V_{cal}	V_{exp}	V_{cal}	V_{exp}	V_{cal}	P (bar)	V_{exp}	V_{cal}
1	1.0843	1.0835	1.0119	1.0114	1.0212	1.0208	1.000	1.000	1	1.3751	1.3751
980	0.9415	0.9410	0.9741	0.9730	0.9506	0.9503			344.6	1.3224	1.3219
1960	0.8845	0.8841	0.9439	0.9434	0.9081	0.9078	0.958	0.958	689.1	1.2852	1.2852
2940	0.8490	0.8485	0.9201	0.9194	0.8786	0.8776			1033.6	1.2571	1.2571
3920	0.8222	0.8226	0.8997	0.8992	0.8545	0.8541	0.932	0.932	1722.8	1.2157	1.2151
4900	0.8014	0.8024	0.8824	0.8820	0.8443	0.8351			2411.8	1.1838	1.1838
5880	0.7850	0.7858	0.8668	0.8669	0.8178	0.8190	0.911	0.913	3101.0	1.1588	1.1588
6860	0.7729	0.7718	0.8530	0.8536	0.8038	0.8052			4134.6	1.1286	1.1288
7840	0.7592	0.7596	0.8407	0.8416	0.7917	0.7931	0.893	0.899	5168.2	1.1041	1.1046
8820	0.7474	0.7489	0.8296	0.8308	0.7807	0.7823			6546.4	1.0776	1.0781
9800			0.8192	0.8209	0.7703	0.7726	0.879	0.887	7924.6	1.0533	1.0563
10780					0.7606	0.7638			9302.8	1.0365	1.0376
11760					0.7521	0.7557	0.866	0.877	10336.5	1.0244	1.0252

[a] References are shown in *Table 6*

[b] Calculated values are obtained from equation (17)

Table 5 Values used in the calculations for argon at various temperatures[a]

	β_T				α_P			
T (K)	$P_0(T)$ (bar)	$A(T)$ (bar)	m_0[b]	β_0	$P_0(T)$ (bar)	$B(T)$ (bar)	n_0[c]	β_0
90	333	0.02608	0.803	2.04	349	0.06235	0.445	4.04
100	265	0.03200	0.822	2.31	247	0.08025	0.493	37.4
110	187	0.03907	0.844	2.71	164	0.08986	0.520	−12.8
120	111	0.04352	0.852	2.89	86.8	0.08786	0.518	−14.4
130	46.5	0.05099	0.870	3.34	27.5	0.08349	0.518	−14.4
140	−8.0	0.05471	0.873	3.43	−17.7	0.08272	0.517	−15.2
150	−43.5	0.07354	0.907	4.88	−53.2	0.07996	0.511	−23.2

[a] Critical temperature and pressure for argon are $T_c = 150.86$ K and $P_c = 48.98$ bar[20]
[b] $m_0 = 2\beta_0/(2\beta_0 + 1)$
[c] $n_0 = \beta_0/(2\beta_0 + 1)$

Table 6 Values used in calculations of specific volume under pressure

	m_0	$D(T) = A(T)/(1 - m_0)$	C_0	$P_0(T)$ (bar)	Temp. (°C)	Pressure range (kbar)	β_0	V_0 (cm^3 g^{-1})	Ref.
CCl_4	0.96	2.082	2.727	847	50	2.0	12.0	0.6511	22
CS_2	0.818	0.1602	0.5768	1138	25	2.0	2.25	0.7965	22
H_2O	0.983	7.756	8.904	3370	50	10.0	28.9	1.0119	1
Isopentane	0.924	0.817	1.299	445	25	1.2	6.08	1.6266	22
Isopentane	0.936	1.097	1.597	355	50	9.0	7.31	1.0843	1
n-Heptane	0.8296	0.1771	0.4394	206	120	1.2	2.43	1.007	24
Ethyl alcohol	0.936	1.155	1.816	1180	20	12.0	7.31	1.0212	1
Glycerine	0.987	5.288	5.857	2600	30	12.0	38.0	1.000	1
n-Hexadecane	0.7686	0.06863	0.2762	409	120	1.2	1.66	1.421	24
n-Octadecane	0.781	0.07508	0.2693	340	135	5.5	1.78	1.4215	23
Chlorobenzene	0.889	0.3970	0.8496	950	95	11.0	4.00	1.1013	1
9-*n*-Octyl heptadecane	0.855	0.2172	0.5424	550	135	10.0	3.05	1.7351	23
PS	0.810	0.1382	0.5108	970	248.9	2.0	2.13	1.079	7, 18
PNBMA	0.790	0.07677	0.3367	1140	82.3	2.0	1.88	0.9840	6
PE (hi. M_w)	0.930	0.7874	1.247	712	187.8	2.0	6.64	1.3306	11
PE (branched)	0.792	0.09068	0.3467	630	172.0	2.0	1.90	1.3037	11

DISCUSSION

An important approximation used in this work is

$$P/\gamma_v T \ll 1 \qquad (18)$$

which is examined using equation (16) by

$$(P/\gamma_v T)/(P/\gamma_v T)_{1\,\mathrm{bar}} = (1 + P_0)^{\beta_0/(2\beta_0+1)}P^{(\beta_0+1)/(2\beta_0+1)} \qquad (19)$$

where $(P/\gamma_v T)_{1\,\mathrm{bar}}$ is a value at 1 bar and $P \gg P_0$ is used. For $\beta_0 = 2.0$, equation (19) becomes

$$(P/\gamma_v T)/(1/\gamma_v T)_{1\,\mathrm{bar}} = (1 + P_0)^{0.4}P^{0.6}$$

which gives a value of 1200 for $P_0 = 50$ bar and $P = 10$ kbar and 300 for $P_0 = 50$ bar and $P = 1$ kbar. The experimental value of $P/\gamma_v T$ for argon at 130 K is 0.64 at 2026 bar. Therefore $P/\gamma_v T \ll 1$ is satisfied over the limited high pressure range.

It is interesting to refer to the other useful equation of state under pressure. The Tait equation is given by[6]

$$1 - V(P)/V(P_0) = c \ln\{1 + P/B^*(T)\} \qquad (20)$$

where $B^*(T)$ is a function of temperature: $B^*(T) \propto \exp(-B_1 T)$. Wilhelm[21] proposed a modified Tait equation with two parameters:

$$V(P)/V(P_0) = (1 + np\beta_{T,0})^{-n^{-1}} \qquad (21)$$

where P_0 is a reference pressure conveniently taken as 1 bar, $p = P - P_0$, $\beta_{T,0}$ is β_T at P_0 and n is a constant ranging from 9 to 11 given by $n = -(\partial\beta_T/\partial P)_T/\beta_T^2$, while equation (17) in this work is expressed approximately over the range $V/V_0 \lesssim 1$ using $\ln(V/V_0) \sim -(1 - V/V_0)$ by

$$V(P)/V(P_0) = -D(T)(P + P_0(T))^{1-m_0} + C_0 + 1 \qquad (22)$$

where $m_0 = 2\beta_0/(2\beta_0 + 1)$ and $V_0 = V(P_0)$. The β_T for the Tait equation is given by

$$-(1/V_0)(\partial V/\partial P)_T \sim \{P + B^*(T)\}^{-1} \qquad (23)$$

and for the Wilhelm equation it is given by

$$-(1/V_0)(\partial V/\partial P)_T \sim (1 + np\beta_{T,0})^{-n^{-1}-1} \qquad (24)$$

or

$$-(1/V)(\partial V/\partial P)_T = \beta_T = (\beta_{T,0}^{-1} + np)^{-1} \qquad (25)$$

Equation (25) is essentially the same as equation (23), while our equation given by equation (14) or equation (22) is expressed by

$$\beta_T \sim \{P + P_0(T)\}^{-m_0} \qquad (26)$$

which is a more general form including the Tait equation with $m_0 = 1.0$.

Bridgman[1] discovered that the thermal expansion $(\partial V/\partial T)_P$ decreases with increasing temperature at a pressure higher than a certain pressure such as 3000–4000 bar and therefore

$$(\partial\alpha_P/\partial T)_P = -\alpha_P^2 + V^{-1}(\partial^2 V/\partial T^2)_P < 0$$

due to $(\partial^2 V/\partial T^2)_P < 0$. According to equation (15), the temperature derivative of α_P at constant pressure is expressed by

$$
\begin{aligned}
(\partial\alpha_P/\partial T)_P = (P + P_0(T))^{-n_0-1} \\
\times [\{\mathrm{d}B(T)/\mathrm{d}T\}\{P + P_0(T)\} \\
- B(T)n_0\{\mathrm{d}P_0(T)/\mathrm{d}T\}] \qquad (27)
\end{aligned}
$$

The first term on the right of equation (27) is negative because $\mathrm{d}B(T)/\mathrm{d}T < 0$ and the second is positive because $\mathrm{d}P_0(T)/\mathrm{d}T < 0$ for argon (see *Table 5*). The pressure at which the sign of $(\partial\alpha_P/\partial T)_P$ changes from positive to negative is estimated using the data for $B(T)$ and $P_0(T)$ for argon, which gives about 1.6 kbar at 100 K if $P_0(T)$ is approximated by $P_0(T) \sim 1/T$ and $B(T) \sim \exp(-aT)$.

It was shown in previous work[19] that the function of P along the critical isotherms is given by

$$|P - P_c| \sim |V_c - V|^{2\beta_0+1} \sim |T_c - T|^{(2\beta_0+1)/3} \qquad (28)$$

and

$$\beta_T \sim |T_c - T|^{-2\beta_0/3} \qquad (29)$$

and therefore

$$\beta_T \sim |P - P_c|^{-2\beta_0/(2\beta_0+1)} \qquad (30)$$

where the relation $|V_c - V| \sim |T_c - T|^{1/3}$ is used. The behaviour of β_T in the critical region speculated by equation (14) is also the same as equation (30) because $P_0(T)$ approaches the critical pressure P_c with a negative sign, as shown in *Table 5*. According to the scaling law, the critical index in equation (30) is $\beta_T \sim |P - P_c|^{-0.775}$ with $\gamma = 1.24$ and $\delta = 4.8$, which are experimental values[20], while that in equation (30) is -0.80 for $\beta_0 = 2.0$.

The difference between values of β_0 determined by β_T and by α_P was observed in argon, as shown in *Table 5*, while the difference between $P_0(T)$ obtained from β_T and α_P is small and may be attributed to the error caused by the approximation in calculation and the experimental error of data. Values of β_0 were determined by $\beta_0 = m_0/2(1 - m_0)$ from m_0 obtained from data for β_T, while values were determined by $\beta_0 = n_0/(1 - 2n_0)$ from n_0 obtained from α_P. We speculate that negative values of β_0 determined from n_0 in *Table 5* are not correct because they are determined erratically due to $n_0 \sim 0.5$ and $\beta_0 = n_0/(1 - 2n_0)$, while β_0 values determined from m_0 are correct. Values of β_0 calculated from m_0 are shown in *Table 6*, where β_0 ranges from 1.0 to ~ 3.0 except for alcohols, water, isopentane and PE (high M_w). We believe that β_0 is an important index in understanding the fundamental properties of liquids. Although β_0 seems to be dependent on temperature in *Table 5*, this may be attributed to the reason that the approximation $P/\gamma_v T \ll 1$ is not good over the higher temperature range near T_c where $\gamma_v T$ becomes smaller. It is suggested from the pressure dependence of $P/\gamma_v T$ in equation (19) that there is a pressure at which $\gamma_v T$ is equal to P in the liquid state where the liquid at the pressure behaves in the same way as an ideal gas because both satisfy the relation $P = \gamma_v T$.

It is emphasized in this work that the functional form of V, β_T and α_P with respect to pressure at constant temperature are determined first using the homogeneous function method, and the constants are then determined using the experimental data. For example, $A(T)$, $P_0(T)$ and $2\beta_0/(2\beta_0 + 1)$ in equation (14) can be determined in principle by three values of β_T at different pressures. Therefore there is no adjustable parameter in this work. Note also that the quantities $P_0(T)$ and $A(T)$ for β_T in equation (14) and $B(T)$ for α_P in equation (15) are known functions expressed by T, V and $A_0(T)$, which is defined by

$$A_0(T) = c_1(a_0^{-1} - \alpha_0^{-1})T\{\exp(\alpha_0^{-1}I_0)\}V_c^{-1} \qquad (31)$$

For example,

$$P_0(T) = A_0(T)TX_0^{2\beta_0+1}/(2\beta_0 + 1) - P(V_0)$$

and therefore $P_0(T_c)$ is equal to $-P(V_c) = -P_c$ due to $X_0 = 0$ at $V = V_c$, which agrees with the experimental results in *Table 5*. A detailed examination of the equation of state in this work with respect to the temperature dependence of α_P and β_T at constant pressure is given elsewhere[19].

REFERENCES

1 Bridgman, P. W. 'The Physics of High Pressure', G. Bell and Sons Ltd, London, 1949

2 Streett, W. B. *Physica* 1974, **76**, 59

3 Thoen, J., Vangeel, E. and Van Dael, W. *Physica* 1969, **45**, 339

4 Streett, W. B. and Costantino, M. S. *Physica* 1974, **75**, 283

5 Crawford, R. K. and Daniels, W. B. *J. Chem. Phys.* 1969, **50**, 3171

6 Olabisi, O. and Simha, R. *J. Appl. Polym. Sci.* 1977, **21**, 149

7 Hellwege, K. H., Knappe, W. and Lehmann, P. *Kolloid Z. Z. Polym.* 1962, **183**, 110

8 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507

9 Simha, R. and Somcynsky, T. *Macromolecules* 1969, **2**, 342

10 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 211

11 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 206

12 Jain, R. K. and Simha, R. *J. Chem. Phys.* 1980, **72**, 4909

13 Nanda, V. S. and Simha, R. *J. Chem. Phys.* 1964, **41**, 3870

14 Nanda, V. S., Simha, R. and Somcynsky, T. *J. Polym. Sci. C* 1966, **12**, 277

15 Dee, G. T. and Walsh, D. J. *Macromolecules* 1988, **21**, 811

16 Dee, G. T. and Walsh, D. J. *Macromolecules* 1988, **21**, 815

17 Iwai, Y. and Arai, Y. *Macromolecules* 1985, **18**, 2775

18 McGowan, J. C. *Polymer* 1969, **10**, 841

19 Saeki, S., Tsubokawa, M. and Yamaguchi, T. *Polymer* 1988, **29**, 123

20 Rowlinson, J. S. and Swinton, F. L. 'Liquids and Liquid Mixtures', Butterworth Scientific, London, 1982

21 Wilhelm, E. *J. Chem. Phys.* 1975, **63**, 3379

22 Mopsik, F. *J. Chem. Phys.* 1969, **50**, 2559

23 Cutler, W. G., McMickle, R. H., Webb, W. and Schlessler, R. W. *J. Chem. Phys.* 1958, **29**, 727

24 Boelhouwer, J. W. M. *Physica* 1960, **26**, 1021