Semi-empirical equation of state for polymers and simple liquids in non-critical and critical regions

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The semi-empirical equation of state for the polymers polystyrene (PS), polyisobutylene (PIB) and polydimethyl siloxane (PDMS) and the simple liquids benzene, n-heptane, carbon tetrachloride and argon at a negligible external pressure has been determined using the experimental data of thermal pressure coefficient γ_v, molar volume V and thermal expansion coefficient α_p. The equation of state obtained in this work is expressed by $P=(X^{\beta_0}/V)\{c_1\exp(\alpha_0^{-1}I_0)T-c_0\exp(a_0^{-1}I_0)\}$, where $X=(V_c-V)/V$ and $I_0=\int_{V_c}^{V} X^{\beta_0}/V\,\mathrm{d}V$, V_c is the critical volume and $\alpha_0, \beta_0, a_0, c_1$ and c_0 are constants determined experimentally. We have obtained good agreement between the values of α_p and γ_v calculated and observed, within 1–2% over a wide temperature range. The semi-empirical equation of state in the critical region is expressed by $V_c-V\propto(T_c-T)^{0.33}$, $P-P_c\propto(V_c-V)^{5.0}$, $\beta_T^{-1}\propto(T_c-T)^{1.33}$ and $\alpha_p^{-1}\propto(T_c-T)^{0.67}$ for $\beta_0=2.0$, which agrees semi-quantitatively with the experimental critical indices.

(Keywords: equation of state; polymer; simple liquids; non-critical region; critical region; critical indices)

INTRODUCTION

The equation of state for polymers and simple liquids is very important in characterizing volumetric properties of liquids over wide ranges of temperature and pressure. It is also useful in predicting the thermodynamic properties of liquid mixtures such as phase separation. Extensive studies on the equation of state have been made by Prigogine *et al.*[1], Flory *et al.*[2], Simha *et al.*[3] and Patterson *et al.*[4] Flory *et al.*[2] have derived the reduced equation of state using the van der Waals model for the internal energy and the Tonks model for the entropy in the liquid state. In a previous work we examined Flory's equation of state and found that the van der Waals model and the Tonks model are useful only over a limited temperature range below the boiling point of the liquid[5]. Deviations of values of α_p, the thermal expansion coefficient, and γ_v, the thermal pressure coefficient, calculated by the Flory theory from experimental values occur over temperatures higher than the boiling point of the liquid. However, it has been recognized that the main thermodynamic properties of polymer solutions and simple liquid mixtures are explained through differences in α_p and γ_v between the components in solution, which can be evaluated by the reduced equation of state of Flory *et al.*[6]

On the other hand, extensive investigations of the equation of state in the critical region have been made. In 1945 Guggenheim proposed a well-known empirical equation[7]:

$$(\rho_l-\rho_g)/\rho_c=(7/2)(1-T/T_c)^{1/3} \tag{1}$$

where ρ_l is the density of the liquid, ρ_g the density of the gas, ρ_c the critical density and T_c the critical temperature. It is also found that the index of equation (1) corresponding to the van der Waals equation is $\frac{1}{2}$, which is not consistent with the experimental value. The scaling law and the renormalization group method have drawn much attention and played an important role in our understanding of the critical phenomena[8–12].

In this work we have tried to derive a semi-empirical equation of state for polymers and simple liquids which allows quantitative prediction of experimental data for α_p and γ_v over the wide temperature range in the non-critical region and the experimental critical indices in the critical region. We selected three polymers, polystyrene, polyisobutylene and polydimethyl siloxane, and four simple liquids, benzene, n-heptane, carbon tetrachloride and argon, for which experimental data over a wide temperature range are available.

SEMIEMPIRICAL EQUATION OF STATE IN NON-CRITICAL REGION

The equation of state is expressed using the thermodynamic equation of state

$$(\partial E/\partial V)_T=\gamma_v T-P \tag{2}$$

and therefore

$$P=\gamma_v T-(\partial E/\partial V)_T \tag{3}$$

The equation of state can be determined if the functions $\gamma_v T-P$ and γ_v are determined. The internal energy $E(V,T)$ and entropy $S(V,T)$ are related to $\gamma_v T-P$ and γ_v through the following equations based on thermodynamics[13]:

$$E(V,T)=E(0.0)+\int_0^T C_v\,\mathrm{d}T+\int_{V(0,0)}^{V}(\partial E/\partial V)_T\,\mathrm{d}V \tag{4}$$

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and

$$S(V,T)=S(0,0)+\int_0^T C_v/T\,\mathrm{d}T+\int_{V(0,0)}^{V}\gamma_v\,\mathrm{d}V \tag{5}$$

where $E(0,0)$ is a value at $T=0$ and $V=V(0,0)$; $V(0,0)$ a value extrapolated to $T=0$ and $P=0$; $S(0,0)$ a value at $T=0$ and $V=V(0,0)$; C_v the heat capacity at constant volume and γ_v the thermal pressure coefficient. The equation of state is related to $E(V,T)$ and $S(V,T)$ through $(\partial E/\partial V)_T$ and γ_v, not to C_v and C_v/T, in equations (4) and (5) if C_v is a function of temperature only. In this calculation we have used two assumptions. One is that $E(V,T)$ and $S(V,T)$ are expressed by a summation of functions of temperature and volume, which means that $E(V,T)=E(V)+E(T)$ and $S(V,T)=S(V)+S(T)$. The other is that $E(V)$ and $S(V)$ are expressed by homogeneous functions of $V/(V_c-V)$. The variable $V/(V_c-V)$ is useful in predicting a divergence of α_p and β_T at the critical point because it also diverges at the critical point. The expressions for $E(V,T)$ and $S(V,T)$ in this work are given by

$$E(V,T)=E(T)+a_0(\gamma_vT-P)V\{V/(V_c-V)\}^{b_0} \tag{6}$$

and

$$S(V,T)=S(T)+\alpha_0\gamma_vV\{V/(V_c-V)\}^{\beta_0} \tag{7}$$

where V_c is the critical volume, a_0, b_0, α_0 and β_0 are constants, $E(T)$ and $S(T)$ are temperature-dependent terms in $E(V,T)$ and $S(V,T)$, respectively, and the dimensions of energy and entropy are taken into account in the equations. Although both $E(V,T)$ and $S(V,T)$ seem to diverge to infinity at the limit of $V=V_c$, the divergences are cancelled by functions of γ_vT-P and γ_v, which approach zero at the critical point (see equations (15) and (16)).

The function γ_vT-P is calculated using equations (2) and (6):

$$\begin{aligned}\gamma_vT-P&=a_0\{\partial(\gamma_vT-P)/\partial V\}_TV\{V/(V_c-V)\}^{b_0}\\&\quad+a_0(\gamma_vT-P)[\{(b_0+1)V_c-V\}/(V_c-V)]\{V/(V_c-V)\}^{b_0}\end{aligned} \tag{8}$$

By dividing equation (8) by $(\gamma_vT-P)a_0V\{V/(V_c-V)\}^{b_0}$, which is non-zero, we obtain

$$\begin{aligned}a_0^{-1}\{(V_c-V)/V\}^{b_0}/V&=\{\partial(\gamma_vT-P)/\partial V\}_T/(\gamma_vT-P)\\&\quad+\{(b_0+1)V_c-V\}/\{V(V_c-V)\}\end{aligned} \tag{9}$$

Then, integrating equation (9) with respect to volume at constant temperature, we obtain

$$\gamma_vT-P=c_0[\{(V_c-V)/V\}^{b_0}/V]\exp(a_0^{-1}I_{b_0}) \tag{10}$$

where I_{b_0} is defined by

$$I_{b_0}=\int_{V_c}^{V}\{(V_c-V)/V\}^{b_0}/V\,\mathrm{d}V \tag{11}$$

and c_0 is an integration constant and a function of temperature in general. However, we take c_0 to be constant in this work because γ_vT-P is a function of volume only, because $E(V,T)=E(T)+E(V)$. The equation for γ_v is derived using equation (7) and $\gamma_v=(\partial S/\partial V)_T$ by a similar procedure to that for γ_vT-P, and is given by

$$\gamma_v=c_1[\{(V_c-V)/V\}^{\beta_0}/V]\exp(\alpha_0^{-1}I_{\beta_0}) \tag{12}$$

where I_{β_0} is defined by

$$I_{\beta_0}=\int_{V_c}^{V}\{(V_c-V)/V\}^{\beta_0}/V\,\mathrm{d}V \tag{13}$$

and c_1 is a constant for the same reason as that for c_0. The equation of state is derived from equations (3), (10) and (12) as

$$\begin{aligned}P&=c_1[\{(V_c-V)/V\}^{\beta_0}/V]\exp(\alpha_0^{-1}I_{\beta_0})T\\&\quad-c_0[\{(V_c-V)/V\}^{b_0}/V]\exp(a_0^{-1}I_{b_0})\end{aligned} \tag{14}$$

The internal energy and entropy are given using equations (6), (7), (10) and (12) by

$$E(V,T)=E(T)+c_0a_0\exp(a_0^{-1}I_{b_0}) \tag{15}$$

and

$$S(V,T)=S(T)+c_1\alpha_0\exp(\alpha_0^{-1}I_{\beta_0}) \tag{16}$$

It is obvious that neither $E(V,T)$ nor $S(V,T)$ diverges at the critical point if $E(T)$ and $S(T)$ do not diverge at the critical point. It is noteworthy that values of γ_vT-P, γ_v and P calculated in this work are zero at $V=V_c$ in the case of $b_0>0$ and $\beta_0>0$ (see equations (10), (12) and (14)), while the observed values of these quantities at $V=V_c$ are not zero. The equation of state in the critical region is discussed below.

SEMI-EMPIRICAL EQUATION OF STATE IN THE CRITICAL REGION

First we must solve the discrepancy at the critical point between the prediction of equation (14) and experimental results. It is useful to define the following quantities:

$$\tilde{P}=P-P_c \tag{17}$$

and

$$\tilde{\gamma}_v\tilde{T}=\gamma_vT-\gamma_{v,c}T_c \tag{18}$$

Equation (3) is rewritten using equations (17) and (18) as

$$\tilde{P}=\tilde{\gamma}_v\tilde{T}-(\tilde{\gamma}_v\tilde{T}-\tilde{P}) \tag{19}$$

If the expressions for $E(V)$ and $S(V)$ in equations (6) and (7) are redefined by

$$\tilde{E}(V)=E(V)-(\gamma_{v,c}T_c-P_c)V \tag{20}$$

and

$$\tilde{S}(V)=S(V)-\gamma_{v,c}V \tag{21}$$

the following equations are derived:

$$(\partial\tilde{E}/\partial V)_T=\tilde{\gamma}_v\tilde{T}-\tilde{P} \qquad (22)$$

and

$$(\partial\tilde{S}/\partial V)_T=\tilde{\gamma}_v=\gamma_v-\gamma_{v,c} \qquad (23)$$

Then we can obtain the same equations as those derived before, except for the definition of P, γ_vT-P and γ_v. Therefore, the discrepancy at the critical point mentioned before is resolved because $\tilde{P}$, $\tilde{\gamma}_v\tilde{T}-\tilde{P}$ and $\tilde{\gamma}_v$ must be zero at the critical point due to their definitions (see equations (17) and (18)).

EMPIRICAL DETERMINATION OF INDICES IN EQUATION (14)

The thermal expansion coefficient α_p calculated from equation (14) is given by

$$\begin{aligned}(\alpha_pT)^{-1}&=\beta_0V/(V_c-V)+\beta_0+1-\alpha_0^{-1}V(\partial I_{\beta_0}/\partial V)_T\\&\quad-\{b_0V/(V_c-V)+b_0+1-a_0^{-1}V(\partial I_{b_0}/\partial V)_T\}\\&\quad\times(1-P/\gamma_vT) \qquad (24)\end{aligned}$$

For $P\ll\gamma_vT$, $(\alpha_pT)^{-1}$ in equation (24) is approximated by

$$\begin{aligned}(\alpha_pT)^{-1}&=(\beta_0-b_0)\{V_c/(V_c-V)\}-\alpha_0^{-1}V(\partial I_{\beta_0}/\partial V)_T\\&\quad+a_0^{-1}V(\partial I_{b_0}/\partial V)_T \qquad (25)\end{aligned}$$

Because $(\alpha_pT)^{-1}\rightarrow0$ in the limit $V\rightarrow V_c$, β_0-b_0 in the first term on the right-hand side of equation (25) must be zero, and we obtain

$$(\alpha_pT)^{-1}=\{(V_c-V)/V\}^{\beta_0}(a_0^{-1}-\alpha_0^{-1}) \qquad (26)$$

where the equation obtained from equation (11)

$$\begin{aligned}(\partial I_{\beta_0}/\partial V)_T&=(\partial I_{b_0}/\partial V)_T\\&=\left|\{(V_c-V)/V\}^{\beta_0}/V\right|_{V_c}^{V}\\&=\{(V_c-V)/V\}^{\beta_0}/V\end{aligned}$$

is used. Equation (26) is valid for both non-critical and critical regions because the difference between P and $\tilde{P}$ does not affect equation (26).

Using the relation $\beta_0=b_0$, we obtain expressions for γ_vT-P and γ_v as follows:

$$\gamma_vT-P=c_0[\{(V_c-V)/V\}^{\beta_0}/V]\exp(a_0^{-1}I_0) \qquad (27)$$

and

$$\gamma_v=c_1[\{(V_c-V)/V\}^{\beta_0}/V]\exp(\alpha_0^{-1}I_0) \qquad (28)$$

where I_0 is defined by

$$I_0=\int_{V_c}^{V}\{(V_c-V)/V\}^{\beta_0}/V\,\mathrm{d}V \qquad (29)$$

The equation of state for the non-critical and critical regions is

$$\begin{aligned}P&=c_1[\{(V_c-V)/V\}^{\beta_0}/V]\exp(\alpha_0^{-1}I_0)T\\&\quad-c_0[\{(V_c-V)/V\}^{\beta_0}/V]\exp(a_0^{-1}I_0) \qquad (30)\end{aligned}$$

The integral in equation (29) has been evaluated using the approximation

$$I_0=K-\delta_0\ln\{(V_c-V)/V\} \qquad (31)$$

where K and δ_0 are constants. In the approximation we intended to express γ_vT-P and γ_v as functions of $(V_c-V)/V$. From equations (27) and (28), the functions of γ_vT-P and γ_v are expressed using equation (31) by

$$\gamma_vT-P=c_0^*\{(V_c-V)/V\}^{(\beta_0-\delta_0a_0^{-1})}/V \qquad (32)$$

and

$$\gamma_v=c_1^*\{(V_c-V)/V\}^{(\beta_0-\delta_1\alpha_0^{-1})}/V \qquad (33)$$

where $c_0^*=c_0\exp(Ka_0^{-1})$ and $c_1^*=c_1\exp(K\alpha_0^{-1})$ are constants. It is interesting to express temperature T as a function of volume. From equations (32) and (33) and the approximation

$$\gamma_vT-P=\gamma_vT(1-P/\gamma_vT)\approx\gamma_vT$$

we obtain

$$\mathrm{T}=(c_0^*/c_1^*)\{V/(V_c-V)\}^{\delta_0(a_0^{-1}-\alpha_0^{-1})} \qquad (34)$$

and therefore

$$\gamma_v=c_0^*\{(V_c-V)/V\}^{(\beta_0-\delta_0a_0^{-1})}/VT \qquad (35)$$

Indices such as β_0 and $\delta_0a_0^{-1}$ have been evaluated from equations (26) and (32) by a log–log plot:

$$\ln(\alpha_pT)^{-1}=\beta_0\ln X+\ln(a_0^{-1}-\alpha_0^{-1}) \qquad (36)$$

and

$$\ln(\gamma_vT-P)-\beta_0\ln X+\ln V=\ln c_0^*-\delta_0a_0^{-1}\ln X \qquad (37)$$

where X is defined by

$$X=(V_c-V)/V \qquad (38)$$

For polymers it is necessary to evaluate V_c in determining β_0 if equation (36) is used. We estimated β_0 first and then determined V_c for polymers as follows. Equation (36) is rewritten using the approximation $V/V_c\ll1$ as

$$\ln(\alpha_pT)^{-1}=\beta_0\ln V_c-\beta_0\ln V+\ln(a_0^{-1}-\alpha_0^{-1}) \qquad (39)$$

Values of V_c for polymers are estimated using equation (36) and β_0 by trial and error.

RESULTS

Experimental data for α_p, γ_v and V are available for the simple liquids benzene[14], n-heptane[14], carbon tetrachloride[14] and argon[14] and the polymers polystyrene[15], polyisobutylene[16] and polydimethyl siloxane[17]. Data in the literature for α_p, γ_v and V for the simple liquids are obtained at pressures higher than the saturated vapour pressure. Therefore the pressure effect on the quantities must be taken into account when data for a temperature above the boiling point are used to determine indices such as β_0.

The plots for equations (36) and (37) are shown in *Figures 1–3*, where linearity is observed over the wide range of X. The indices and constants obtained in this work are summarized in *Table 1*. Numerical comparisons for $\gamma_v T - P$, γ_v and $(\alpha_p T)^{-1}$ values calculated in this work and observed are given in *Table 2*, in which $\gamma_v T - P$ and γ_v are calculated using equations (32) and (35) and $(\alpha_p T)^{-1}$ is calculated using equation (26).

It is interesting to derive the critical indices from the equation of state obtained in this work. From equation (26) we obtain

$$\ln T = (a_0^{-1} - \alpha_0^{-1}) \int_{V_c}^{V} X^{\beta_0}/V \, \mathrm{d}V \qquad (40a)$$

or

$$T = (c_0/c_1)\exp\{(a_0^{-1} - \alpha_0^{-1}) I_0\} \qquad (40b)$$

The expression for γ_v without using the approximation of equation (31) is derived from equation (30) as

$$\gamma_v = c_1 X^{\beta_0} V^{-1} \exp(\alpha_0^{-1} I_0) \qquad (41)$$

and therefore the isothermal compressibility β_T is given using $\beta_T = \alpha_p/\gamma_v$ by

$$\beta_T = \{1/c_1(a_0^{-1} - \alpha_0^{-1})\}(V/T) X^{-2\beta_0} \exp(-\alpha_0^{-1} I_0) \qquad (42)$$

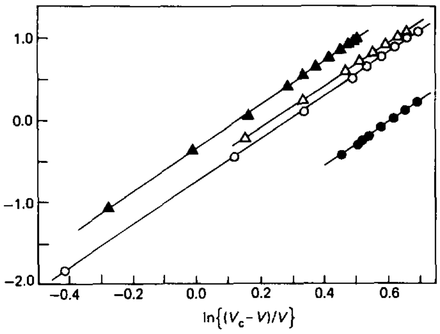

Figure 1 $\ln(\alpha_p T)^{-1}$ *versus* $\ln\{(V_c - V)/V\}$ from equation (36) for benzene (△), n-heptane (○), carbon tetrachloride (●) and argon (▲)

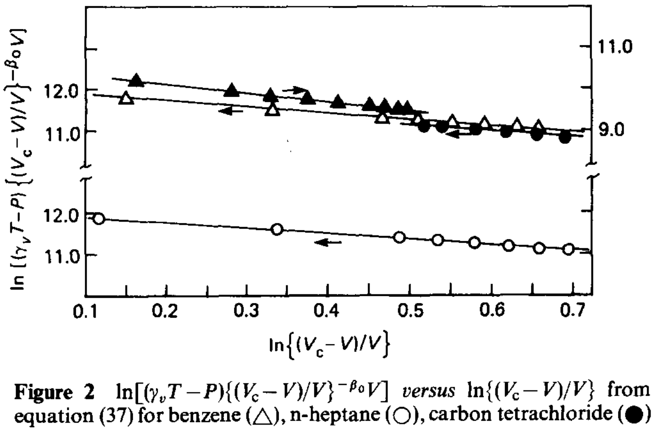

Figure 2 $\ln[(\gamma_v T - P)\{(V_c - V)/V\}^{-\beta_0} V]$ *versus* $\ln\{(V_c - V)/V\}$ from equation (37) for benzene (△), n-heptane (○), carbon tetrachloride (●) and argon (▲)

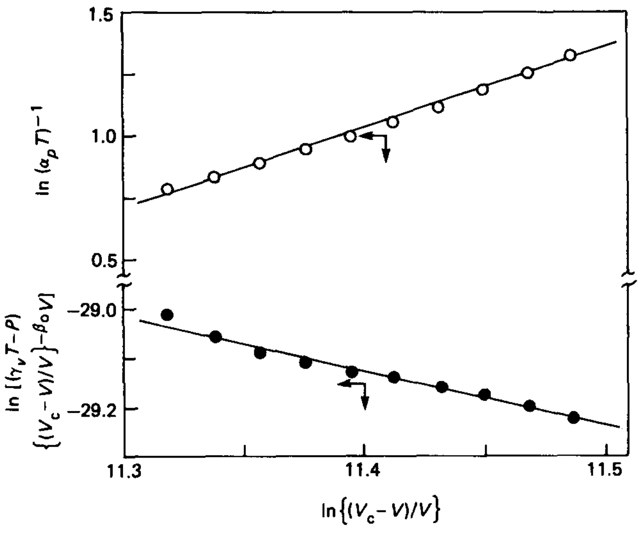

Figure 3 $\ln(\alpha_p T)^{-1}$ *versus* $\ln\{(V_c - V)/V\}$ and $\ln[(\gamma_v T - P) \times \{(V_c - V)/V^{-\beta_0} V]$ *versus* $\ln\{(V_c - V)/V\}$ for polydimethyl siloxane

The function of P along the critical isotherm is given using equation (42) by

$$P = -c_1(a_0^{-1} - \alpha_0^{-1}) T \int_{V_c}^{V} X^{2\beta_0} V^{-2} \exp(\alpha_0^{-1} I_0) \mathrm{d}V \qquad (43)$$

It is convenient to rewrite the above equations in the usual form using an approximation for I_0:

$$I_0 = -\int_0^X X^{\beta_0}/(1+X)\,\mathrm{d}X \qquad (44a)$$

$$\approx -\int_0^X A X^n \,\mathrm{d}X \qquad (44b)$$

$$= -A(n+1)^{-1} X^{n+1} \qquad (44c)$$

Equations (40b), (42) and (43) are expressed using equation (44c) by

$$T = (c_0/c_1)\{1 - A(a_0^{-1} - \alpha_0^{-1}) X^{n+1}/(n+1)\} \qquad (45a)$$

or

$$(T_c - T)/T_c \sim X^{(n+1)} \qquad (45b)$$

while the function of β_T in the critical region is given by

$$\beta_T = \{c_1(a_0^{-1} - \alpha_0^{-1})\}^{-1}(V/T) X^{-2\beta_0}\{1 + A X^{n+1}/\alpha_0(n+1)\} \qquad (46a)$$

$$\sim X^{-2\beta_0} \qquad (46b)$$

$$\sim \{(T_c - T)/T_c\}^{\{-2\beta_0/(n+1)\}} \qquad (46c)$$

Table 1 Indices and constants in equations (26) and (32) determined in this work

	β_0	$\delta_0 a_0^{-1}$	c_0[a] (bar cm^3 mol^{-1})	$a_0^{-1}-\alpha_0^{-1}$	V_c (cm^3 mol^{-1})
Polystyrene	5.22	3.02	5.25×10^{-6}	5.43×10^{-21}	1.0×10^{4}[a]
Polyisobutylene	5.74	4.53	1.10×10^{-2}	3.83×10^{-26}	4.0×10^{4}[a]
Polydimethyl siloxane	3.22	1.09	5.58×10^{-8}	3.20×10^{-16}	10.0×10^{4}[a]
Benzene	2.60	1.60	1.80×10^{5}	0.549	255.3
n-Heptane	2.66	1.60	1.90×10^{5}	0.472	430
Carbon tetrachloride	2.80	1.85	1.84×10^{5}	0.497	276
Argon	2.74	2.23	0.40×10^{5}	0.698	74.6

[a] V_c (cm^3 g^{-1})

Table 2 Comparison of $(\alpha_p T)^{-1}$, $\gamma_v T-P$ and γ_v calculated in this work and observed values for polyisobutylene and n-heptane

	Polyisobutylene						n-Heptane					
	$(\alpha_p T)^{-1}$		$(\gamma_v T-P)$ (10^3 bar)		γ_v (bar K^{-1})		$(\alpha_p T)^{-1}$		$(\gamma_v T-P)$ (10^3 bar)		γ_v (bar K^{-1})	
Temp. (°C)	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	6.46	6.58	3.46	3.49	12.66	12.81	3.025	3.011	2.73	2.78	10.0	10.2
20							2.764	2.725	2.60	2.60	8.88	8.89
25	6.02	6.07	3.39	3.39	11.36	11.37						
40							2.48	2.46	2.44	2.44	7.80	7.80
50	5.60	5.60	3.29	3.29	10.19	10.18						
60							2.21	2.20	2.28	2.27	6.85	6.82
80							1.95	1.96	2.12	2.10	5.99	5.97
100	4.85	4.77	3.07	3.09	8.23	8.28	1.70	1.72	1.96	1.94	5.25	5.22
150	4.18	4.04	2.87	2.90	6.78	6.85	1.14	1.16	1.51	1.51	3.57	3.59
200							0.64	0.64	1.04	1.06	2.22	2.25
250							0.159	0.156	0.50	0.47	1.0	0.902

Table 3 Critical indices calculated in this work and observed

	Exponents	
Property	Obs.	Calc.[a]
V_c-V_l as a function of T_c-T	$\beta=0.32\pm0.01$	0.33
$-(\partial P/\partial V)_T=(\beta_T V)^{-1}$ as a function of T_c-T	$\gamma=1.24\pm0.05$[b]	1.33
$\lvert P-P_c\rvert$ as function of V_c-V_l	$\delta=4.8\pm0.2$	5.0

[a] Calculated using $\beta_0=2.0$, $n=2.0$ and equations (45b), (46c) and (47c)
[b] γ^+ along critical isocore is assumed equal to γ_l^- through orthobaric states of homogeneous fluid (see ref. 14)

The function P along the critical isotherm is given by

$$P=-c_1(a_0^{-1}-\alpha_0^{-1})T\int_{V_c}^{V} X^{2\beta_0}V^{-2}\{1-AX^{n+1}/\alpha_0(n+1)\}\,\mathrm{d}V \tag{47a}$$

$$\approx c_1(a_0^{-1}-\alpha_0^{-1})TV_c^{-1}X^{2\beta_0+1} \tag{47b}$$

$$\sim X^{(2\beta_0+1)} \tag{47c}$$

The function α_p is obtained from equation (26):

$$\alpha_p=T^{-1}(a_0^{-1}-\alpha_0^{-1})^{-1}X^{-\beta_0} \tag{48a}$$

$$\sim\{(T_c-T)/T_c\}^{\{-\beta_0/(n+1)\}} \tag{48b}$$

It is obvious that the critical indices are calculated from β_0 and n. For $\beta_0=2.6$, the integration of equation (44a) is approximated by $n=2$ and $A=0.5$, which gives $I_0=-X^3/6$. It is also true that in the critical region I_0 is approximated to $-X^{\beta_0+1}/(\beta_0+1)$ in equation (44a) because $X\approx0$. In this work we used $n=2.0$ and $\beta_0=2.0$ in calculating the critical indices which are listed in *Table 3*.

It is suggested from this work that the semi-empirical equation of state based on equations (6) and (7) and equation (3) allows quantitative prediction of experimental data for α_p and γ_v over a wide temperature range and semi-quantitative prediction of critical indices. It is also found that the index β_0 plays an important role in the equation of state.

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