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A Cubic Equation of State for High-Pressure Phase Equilibria of Mixtures Containing Polymers and Volatile Fluids

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DISCLAIMER

A Cubic Equation of State for High-Pressure Phase Equilibria of Mixtures Containing Polymers and Volatile Fluids

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ABSTRACT

Generalized van der Waals theory is used to obtain a three-parameter cubic equation of state which is applicable to fluids containing small or large molecules, including polymers. Upon extension to mixtures, the equation of state is used to calculate high-pressure phase equilibria for the ethylene-polyethylene system. The relatively simple equation may be useful for engineering-design calculations for fluid mixtures containing polymers.

INTRODUCTION

An equation of state(EOS) provides a powerful tool for chemical process design. However, most existing EOS are applicable only to mixtures containing volatile fluids. While several authors have presented EOS which may also be used for fluids containing non-volatile, large molecules such as polymers(Beret and Prausnitz, 1975a; Donohue and Prausnitz, 1978; Chien et al., 1983), these equations are often complex and require molecular parameters which are not readily available. The purpose of this paper is to present a simple cubic EOS which is useful for both small and large molecules, and which requires a minimum of experimental information. We derive our EOS from the generalized van der Waals partition function coupled with Prigogine's and Beret's assumptions, and present a new method for calculating pure-component parameters in the EOS. We illustrate application with some calculations for high-pressure phase equilibria for the system ethylene-polyethylene.

GENERALIZED VAN DER WAALS PARTITION FUNCTION

As discussed elsewhere(Prausnitz et al., 1986a), the generalized van der Waals partition function Q for a pure fluid is

$$Q = \frac{1}{N!} \left[\frac{V}{\Lambda^3} \right]^N \left[\frac{V_f}{V} \right]^N \left[\exp\left(\frac{-E_0}{2kT} \right) \right]^N \left[q_{r,v} \right]^N \tag{1}$$

where N is the number of molecules in total volume V at temperature T; Λ is the de Broglie wavelength depending only on temperature and molecular mass; V_f is the free volume; k is Boltzmann's constant; and E_0 represents the potential field experienced by one molecule due to attractive forces from all others. The term $(N!)^{-1}(V/\Lambda^3)^N$ gives the translational contribution of an ideal gas to the partition function. The second and third bracketed terms account for repulsive and attractive forces between molecules. The last term represents the contribution of rotational and vibrational degrees of freedom to the partition function.

To obtain a simple EOS, we assume that the free volume is represented by the approximation of van der Waals:

$$V_f = V - \frac{N}{N_A} b \tag{2}$$

where N_A is Avogadro's number and b is a parameter determined by molecular size. For the potential field, we use the Soave-Redlich-Kwong form (Soave, 1972) (see Appendix 1):

$$E_0 = -\frac{2a}{N_A b} \ln\left(1 + \frac{N}{N_A} \frac{b}{V}\right) \tag{3}$$

where parameter a is dependent on temperature, and parameter b is not. Following Prigogine(1957), $q_{r,v}$ is factored into an internal part and an external part:

$$q_{r,v} = q_{r,v(int)} \cdot q_{r,v(ext)} \tag{4}$$

where $q_{r,v(int)}$ depends only on temperature and $q_{r,v(ext)}$ depends on density. Again following Prigogine, we assume further that the external rotational and vibrational degrees of freedom can be considered as equivalent translational degrees of freedom. Beret(1975a) proposed a function for $q_{r,v(ext)}$ which is consistent with Prigogine's assumption at liquid densities and with the ideal-gas law at low density:

$$q_{r,v(ext)} = \left(\frac{V_f}{V}\right)^{c-1} \tag{5}$$

where 3c is the total number of external degrees of freedom per molecule.

The EOS is obtained from the partition function by

$$p = kT \cdot \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{6}$$

Substitution of Equations (1), (2), (3), (4) and (5) into (6) gives a cubic EOS:

$$p = \frac{RT(v-b+bc)}{v(v-b)} - \frac{a}{v(v+b)} \tag{7}$$

where p is the pressure, v is the molar volume and R is the gas constant. When c=1, Equation (7) reduces to the Soave-Redlich-Kwong EOS. The third parameter c extends the applicability of Equation (7) to systems containing large molecules.

If the potential field E_0 is given by the expression of Peng-Robinson, an EOS similar to Equation (7) is obtained. However, in that event, the EOS is fourth order in volume, as discussed by Kubic(1986).

EOS PARAMETERS FOR VOLATILE FLUIDS

For a volatile fluid, parameters $a_{(T=T_c)}$ and b can be obtained upon using the condition that, at the critical point, $(\partial p/\partial V)_{T_c} = (\partial^2 p/\partial V^2)_{T_c} = 0$. We then obtain

$$a_{(T=T_c)} = a_c = \frac{(1-2D_0+2cD_0+D_0^2-cD_0^2)(1+D_0)^2}{3(1-D_0)^2(2+D_0)} \cdot \frac{R^2T_c^2}{p_c} \tag{8}$$

$$b = \frac{D_0}{3} \cdot \frac{RT_c}{p_c} \tag{9}$$

where D_0 is a function of c:

$$D_0^3 + (6c-3)D_0^2 + 3D_0 - 1 = 0 \tag{10}$$

Regardless of the value of c, Equations (7), (8), (9) and (10) give a critical compressibility factor $z_c=1/3$.

At temperatures other than T_c,

$$a = a_c\alpha(T) \tag{11}$$

where $\alpha(T)$ is a dimensionless function which becomes unity at $T=T_c$. Based on our study of the saturated and PVT properties of n-alkanes(Smith and Srivastava, 1986), we propose

$$\alpha(T) = \frac{\alpha_0(1-T_R^2) + 2T_R^2}{1 + T_R^2} \tag{12}$$

where the reduced temperature T_R is defined by $T_R=T/T_c$ and α_0 is given by

$$\alpha_0 = 1.1920 + 0.11060 \cdot \ln(V_w) + 0.30734\times10^{-3} \cdot V_w \tag{13}$$

where van der Waals volume $V_w(cm^3/mol)$ is calculated by the group-contribution method of Bondi(1968).

The fugacity coefficient for a pure fluid is given by

$$\ln\left(\frac{f}{p}\right)_{pure} = -\ln\frac{p(v-b)}{RT} - \frac{a}{bRT}\ln\left(1+\frac{b}{v}\right) + \left(\frac{pv}{RT}-1\right) - \ln\left(\frac{v-b}{v}\right)^{c-1} \tag{14}$$

where the first three terms on the right-hand side are same as those of the Soave-Redlich-Kwong EOS and only the last term contains parameter c.

Figure 1 shows the relation between α_0 and V_w for n-alkanes from methane to pentadecane; the solid line gives results calculated by Equation (13), while the

points show the best α_0 required to reproduce saturated and PVT properties. Figure 2 shows a plot of $\alpha(T)$ vs. T_R for n-octane. The calculated line is obtained from Equations (12) and (13), while the points were obtained from fitting saturated and PVT properties of n-octane. All of these calculations are based on values of c shown in Table 1. This table also indicates that Equations (7) to (13) are suitable for fitting the saturated and PVT properties of n-alkanes from methane to pentadecane.

RE-FORMULATION OF EOS PARAMETERS FOR APPLICATION TO POLYMERS

Equations(8) - (13) are not useful for polymers because critical properties are not available. In order to apply Equation (7) to polymers as well as volatile fluids, energy parameter a is determined from London's formula for dispersion forces(1937); size parameter b is calculated using the van der Waals volume obtained from Bondi's method; only parameter c is determined from density data.

To calculate parameter a, we assume that [1]a polymer molecule can be divided into equal segments; [2]the potential energy between two adjacent, non-bonded segments is given by London's dispersion formula; and [3]the potential energy of the entire system is pairwise additive. When a polymer molecule consists of r segments, molar volume v and parameters a, b, c of the polymer are related to those of the segment by

$$a = r^2 \cdot a' = r^2[a'^* \cdot f'(\tilde{T})] \tag{15}$$

$$b = r \cdot b'$$

$$c = r \cdot c'$$

$$v = r \cdot v'$$

where $'$ represents segment basis and $*$ designates a close-packed system. The function $f'(\tilde{T})$ depends on reduced temperature $\tilde{T}$ which is the ratio of kinetic energy to potential energy per molecule:

$$\tilde{T} = \frac{ckT}{\varepsilon} \tag{16}$$

where ε is a potential-energy parameter per molecule. Parameter ε(per molecule) is related to potential-energy parameter ε'(per segment) by

$$\varepsilon = r \cdot \varepsilon' = \frac{r}{N_A}\left(\frac{A'^2 \cdot I'}{V_w'^2}\right) \tag{17}$$

where A' is the polarizability of the segment$[cm^3/mol]$, I' is the first ionization

potential of the segment$[cm^3 \cdot bar/mol]$, and V_w' is the van der Waals volume of the segment$[cm^3/mol]$.

As shown in Appendix 2, parameter a'^* in Equation (15) is written as

$$a'^* = 2.9108 \cdot \left(\frac{A'^2 \cdot I'}{V_w'} \right) \tag{18}$$

Function $f'(\widetilde{T})$ is expected to have a universal form for n-alkanes and for linear chain polymers such as polyethylene. This function must meet two boundary conditions: $f'(\widetilde{T}) \to 1$ as $\widetilde{T} = 0$, and $f'(\widetilde{T}) \to 0$ as $\widetilde{T} \to \infty$. A simple function which satisfies these boundary conditions is

$$f'(\widetilde{T}) = \exp(-a_0 \widetilde{T}) \tag{19}$$

where a_0 is a constant determined by reduction of saturated-property and PVT data. Combining Equations (15), (18) and (19) gives

$$a = 2.9108 \cdot \left(\frac{A'^2 \cdot I'}{V_w'} \right) \cdot r^2 \cdot \exp(-a_0 \widetilde{T}) \tag{20}$$

Size parameter b is nearly proportional to the van der Waals volume. Figure 4 shows that, when b is determined from critical data using Equation (9), we obtain

$$b = 1.3768 V_w \tag{21}$$

Equation(21) is used to calculate b for polymers. As in Equation (13), V_w is obtained from Bondi's correlation.

Since parameter c is sensitive not only to molecular size but also to molecular structure, it is difficult to correlate this parameter with other properties. Therefore, for polymers, parameter c is determined from fitting density data over whatever range of temperature and pressure may be available.

Determination of a_0

Parameters c, a_0 and segment number r are determined from saturated and PVT properties for n- C_2, C_3, C_4, C_5 and C_7. In this calculation, polarizability A is calculated from molar refraction which, in turn, is obtained from a group-contribution method using atomic indices of refraction (Nippon Kagakukai, 1984) [†];

[†] Other group-contribution methods for molar refractions are also available (Davies 1965; Dean 1979; Weast 1987).

van der Waals volume V_w is calculated using the group-contribution method of Bondi; and first ionization potential I is obtained from Robinson(1974). Parameters c, a_0 and r are fitted to the saturated volumetric data with the following conditions: [1]$f'(\tilde{T})$ is the same for all compounds, and [2]$(A'^2 \cdot I'/V_w')$ is equal to $(1/r)(A^2 \cdot I/V_w)$ because $A = r \cdot A'$, $V_w = r \cdot V_w'$ and $I = I'$, where A, I, V_w are the quantities on molecular basis.

Table 2 gives values of c and r, and identifies the physical properties required to calculate them. From a plot of $f'(\tilde{T})$ vs. $\tilde{T}$ shown in Figure 5, parameter a_0 is determined:

$$f'(\tilde{T}) = \exp(-2.3731\tilde{T}) \tag{22}$$

Determination of Parameter a

For polymers, parameter a is determined by Equation (20). We obtain $(A'^2 I'/V_w')$ from data for the saturated monomer because the characteristic potential energy of the segment $(A'^2 I'/V_w'^2)$ is almost equal to $(A^2 I/V_w^2)$ of the saturated monomer. Figure 6 shows the relation between the characteristic energy of n-alkanes and the molecular chain length. Since this characteristic energy is almost constant, we assume that, if molecules can be divided into equal segments, the characteristic energy per segment is also constant for a homologous series. This assumption is justified because $A = r \cdot A'$, $V_w = r \cdot V_w'$, and $I = I'$. Similarly, we assume that the characteristic energy per segment of a polymer is equal to that of the saturated monomer. Thus, we have

$$\left(\frac{A'^2 I'}{V_w'^2} \right)_{p.s.} = \left(\frac{A'^2 I'}{V_w'^2} \right)_{s.m.s.} = \left(\frac{A^2 I}{V_w^2} \right)_{sat.m.} \tag{23}$$

where subscripts $p.s.$, $s.m.s.$, $sat.m.$ represent the segment of the polymer, the segment of small molecules such as n-alkanes, and the saturated monomer, respectively. Therefore,

$$\left(\frac{A'^2 I'}{V_w'} \right) = \left(\frac{A^2 I}{V_w^2} \right)_{sat.m.} \cdot V_w' \tag{24}$$

Parameter a_0 in Equation (20) is assumed to be same as that for n-alkanes because the polymers treated in this work are chain molecules similar to n-alkanes. The final equation for parameter a is

$$a_{(polymer)} = 2.9108 \cdot \left(\frac{A^2 I}{V_w^2} \right)_{sat.m.} \cdot V_{w(polymer)} \cdot r \cdot \exp(-2.3731 \cdot \tilde{T}) \tag{25}$$

where $V_{w(polymer)}$ is calculated from molecular weight and from the structural formula of the repeating unit.

Segment number r is determined from the assumption that there are 3.33 carbon atoms per segment. This assumption is derived from fitting n-alkane data. Figure 7 shows a plot of carbon number per segment vs. inverse carbon number for n-C_2, C_3, C_4, C_5, and C_7. The extrapolation of the curve leads to the constant value 3.33 for very large molecules.

Data reduction for polymers

We require the molecular weight to correlate PVT data for a polymer. However, a real polymer generally has a molecular-weight distribution and, therefore, three kinds of average molecular weight are in common use: number-average molecular weight, weight-average molecular weight and viscosity-average molecular weight. As the number-average molecular weight is most closely related to thermodynamic properties(van Krevelen,1976), we calculate the volumetric properties considering the polymer to be monodisperse with the number-average molecular weight.

Volumetric data are fitted for 7 liquid polymers over a wide temperature and pressure range(Hellwege et al., 1962; Passaglia and Martin, 1964; Quach and Simha, 1971; Beret and Prausnitz, 1975b). Calculated results are given in Table 3; properties of the saturated monomers are presented in Table 4. The calculated volumes agree well with experiment for the first four polymers from the top of Table 3. The other three polymers give a somewhat larger deviation, probably because the segments of these polymers deviate from spherical symmetry owing to the large phenyl or acetyl group. Figure 8 shows the relation between (c/r) and carbon number for n-alkanes and polyethylene. The value of (c/r) for polyethylene is on the extension of the line for n-alkanes, indicating that Equation (7) provides a reasonable model for polymeric fluids when the polymer is regarded as a homolog of the saturated monomer.

Extension to Mixtures

When phase α is in equilibrium with phase β at the same temperature and pressure, the equilibrium condition is given by

$$x_i^{\alpha} \cdot \phi_i^{\alpha} \cdot p = y_i^{\beta} \cdot \phi_i^{\beta} \cdot p \tag{26}$$

where x, y are mole fractions in phases α and β, and ϕ is the fugacity coefficient. To calculate fugacity coefficients from Equation (7), we require mixing rules for three parameters a, b, c and the segment number r in the EOS. We assume one-fluid mixing rules:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} = \sum_i \sum_j x_i x_j r_i r_j a_{ij}' \qquad (27)$$

$$= \sum_i \sum_j x_i x_j r_i r_j (1-k_{ij}') \sqrt{a_{ii}' a_{jj}'}$$

$$b_m = \sum_i x_i b_i = \sum_i x_i r_i b_i'$$

$$c_m = \sum_i x_i c_i = \sum_i x_i r_i c_i'$$

$$r_m = \sum_i x_i r_i$$

where a_m, b_m, c_m, r_m represent the mixture-parameters on a molecular basis; b_i, c_i, r_i are the pure-component parameters on a molecular basis; a_{ii}', b_i', c_i' are the pure-component parameters on a segment basis; and k_{ij}' is the binary interaction parameter between polymer segment i and solvent segment j.

From Equations (7) and (27), the fugacity coefficient in the mixture is given by

$$\ln\phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln z \qquad (28)$$

$$= -\ln \frac{p(v-b_m)}{RT} - \frac{1}{RT} \left(\frac{2\sum_j x_j a_{ij}}{b_m} - \frac{a_m b_i}{b_m^2} \right) \ln \left(1+\frac{b_m}{v}\right)$$

$$= - \frac{a_m b_i}{b_m RT(v+b_m)} + \frac{b_i c_m}{v-b_m} - \ln \left(\frac{v-b_m}{v}\right)^{c_i-1}$$

At a given temperature and pressure, equilibrium compositions in both phases can be calculated from Equations (26) - (28) in addition to Equation (7).

Phase Equilibria for Ethylene-Polyethylene

Phase equilibria are calculated for the system ethylene(1)-polyethylene(2) at 403.2K using the numerical method presented by Bonner et al(1974). In this calculation, the polyethylene is assumed to be monodisperse. Table 5 gives pure-component parameters on a segment basis for ethylene and polyethylene. Parameters for ethylene are obtained by fitting saturated properties and PVT properties to the EOS. Figures 9 and 10 show calculated results along with experimental data(Luft and Lindler, 1976; Liu and Prausnitz, 1980). These figures also show the effect of the number-average molecular weight of polyethylene, $\overline{M}_n$, on the phase behavior.

The best value of k_{12} is 0.07 for all calculations with different values of $\overline{M}_n$. The small positive value of k_{12} is reasonable because of the similarity in chemical nature and size between ethylene and a polymer segment. However, the value of k_{12} has a large effect on the phase diagram. When k_{12} is smaller than 0.06, the calculated critical pressure is below 1300 bar. On the other hand, a larger k_{12} causes a strong decrease in the concentration of polyethylene in the ethylene-rich phase.

The molecular weight of polyethylene also has an appreciable influence on the calculation. As the literature gives only the viscosity-average molecular weights (11000 for the polyethylene-rich phase, and 23000 for the ethylene-rich phase), the calculation is made for three values of $\overline{M}_n$. The best calculated results are obtained when $\overline{M}_n$ =9000.

The calculated solubility of polyethylene in ethylene is very small at pressures below 1000 bar for all cases of $\overline{M}_n$. As the system pressure approaches the critical pressure, the solubility increases steeply. The shape of the isothermal solubility curve for the ethylene-rich phase is highly sensitive to $\overline{M}_n$ of polyethylene. On the other hand, the solubility curve for the polyethylene-rich phase is not sensitive to $\overline{M}_n$.

The calculated results indicate that if realistic calculations are to be made for both phases, it is necessary to take the molecular-weight distribution into consideration. In other words, it is not satisfactory to represent the heavy component (polyethylene) as a single component with some average molecular weight. Instead, it is necessary to represent the ethylene-polyethylene system as a multicomponent (not a binary) system. Such multicomponent calculations are now in progress.

CONCLUSION

A new cubic EOS was derived from the generalized van der Waals partition function. The resulting three-parameter EOS is applicable to fluids containing small and large molecules.

The EOS was used to correlate volumetric data of n-alkanes. The results demonstrated the new EOS to be as good or better than the Soave-Redlich-Kwong EOS. To extend the proposed EOS to fluids containing very large molecules (polymers), a new method was developed for determining pure-component parameters. This method uses two adjustable parameters, r and c', for volatile fluids, and only one adjustable parameter c' for polymers. The EOS gave a good correlation of volumetric data for seven polymers.

Phase-equilibrium calculations were made for the system ethylene-polyethylene at 403.2 °K, using the proposed EOS and one-fluid mixing rules with one adjustable binary parameter k_{ij}. When the system is considered to be a pseudo-binary, calculated results for the polymer-rich phase are in good agreement with experiment but those for the ethylene-rich phase are only semi-quantitative. To obtain satisfactory agreement for both phases, it is necessary to take into account the molecular-weight distribution of polyethylene.

ACKNOWLEDGEMENTS

Table 1. Calculated saturated and PVT properties for n-alkanes.
Calculations based on Equations (8)-(14).

| Fluid | Parameter c | Deviation from experiment, % | | | | | |
| | | new EOS | | | SRK EOS | | |
		p^s	v_l^s or v_l	v_g^s	p^s	v_l^s or v_l	v_g^s
CH_4	1.00	2.16	5.22	2.77	1.68	5.52	1.80
C_2H_6	1.20	1.14	6.58	1.21	1.28	8.72	1.40
C_3H_8	1.34	1.22	6.97	1.83	0.73	10.51	1.37
C_4H_{10}	1.51	1.75	4.17	2.50	1.67	9.69	0.72
C_5H_{12}	1.68	1.82	5.98	1.98	1.48	12.76	1.25
C_6H_{14}	1.85	2.31	8.85	3.70	0.90	17.57	1.52
C_7H_{16}	2.02	2.23	7.50	2.80	2.00	16.89	2.64
C_8H_{18}	2.19	1.84	8.17	2.14	1.03	19.03	1.01
C_9H_{20}	2.36	0.40	1.00	0.40	0.71	15.79	0.66
$C_{10}H_{22}$	2.54	0.81	1.35	--	1.18	18.82	--
$C_{11}H_{24}$	2.71	1.08	1.55	--	1.39	19.57	--
$C_{12}H_{26}$	2.88	0.90	1.83	--	3.12	21.50	--
$C_{13}H_{28}$	3.05	2.40	1.73	--	1.69	21.25	--
$C_{14}H_{30}$	3.22	2.00	1.60	--	8.43	21.98	--
$C_{15}H_{32}$	3.39	3.02	1.98	--	1.88	23.63	--
Av. Dev.(%)		1.67	4.30	2.15	1.94	16.22	1.37

Table 2. Parameters in EOS and physical properties when using Equations (15)-(21)

	Parameters in EOS				Physical properties		
	$a'^* \times 10^{-6}$ $(cm^6 \cdot bar/mol^2)$	b (cm^3/mol)	c	r	A (cm^3/mol)	$I \times 10^{-7}$ $(cm^3 \cdot bar/mol)$	V_w (cm^3/mol)
C_2H_6	7.777	37.64	1.18	1.10	2.692	1.109	27.34
C_3H_8	8.245	51.73	1.33	1.44	3.788	1.068	37.57
C_4H_{10}	8.593	65.81	1.52	1.78	4.979	1.013	47.80
C_5H_{12}	8.990	79.90	1.66	2.08	6.104	1.001	58.03
C_7H_{16}	9.795	108.1	1.86	2.60	8.353	0.9841	78.49

Correlation for pure components of n-alkanes is made up to the critical point for vapor pressure,liquid density and vapor density (with relative weights 3:2:1) from methane to nonane, and for vapor pressure and liquid density at atmospheric pressure (with relative weights 3:2) from decane to pentadecane.

Table 3. Calculated results for specific volumes of polymers

Polymer	Range of PVT data		$\bar{M}_n$	Segment number	(c/r)	Deviation (%)
	T(°K)	P(bar)				
PE	413-473	1-1000	25000	535.3	0.57	1.42
PP	263-303	1-700	15700	224.1	0.61	0.94
PIB	333-383	1-1000	36000	385.4	0.41	0.61
PVC	355-370	1-1000	30000	288.3	0.49	0.91
PVAC	333-393	1-1000	84000	586.0	0.59	2.97
PS	413-469	1-800	90700	523.0	0.57	3.45
POMS	432-471	1-800	90700	460.9	0.49	3.56

PE: polyethylene   PP: polypropylene
PIB: polyisobutylene   PVC: polyvinylchloride
PVAC: polyvinylacetate   PS: polystyrene
POMS: poly-o-methystyrene

Table 4. Physical properties of saturated monomers

Polymer	Saturated monomer	A (cm^3/mol)	$I \times 10^{-7}$ $(cm^3 \cdot bar/mol)$	V_w (cm^3/mol)
PE	ethane	2.692	1.109	27.34
PP	propane	3.833	1.068	37.57
PIB	isobutane	4.935	1.040	47.79
PVC	ethylchloride	3.892	1.062	36.14
PVAC	ethylacetate	5.302	0.9880	52.77
PS	ethylbenzene	8.485	0.8510	69.74
POMS	o-methyl-ethylbenzene	9.588	0.8153	80.89

Table 5. Pure-component parameters on segment basis for ethylene and polyethylene

Component	T $(°K)$	Segment number	$a' \times 10^{-6}$ $(cm^6 \cdot bar/mol^2)$	b' (cm^3/mol)	c'
ethylene	403.2	0.91	3.8737	36.13	1.23
polyethylene	403.2	$\bar{M}_n \times 0.02141$	6.9917	46.90	0.57

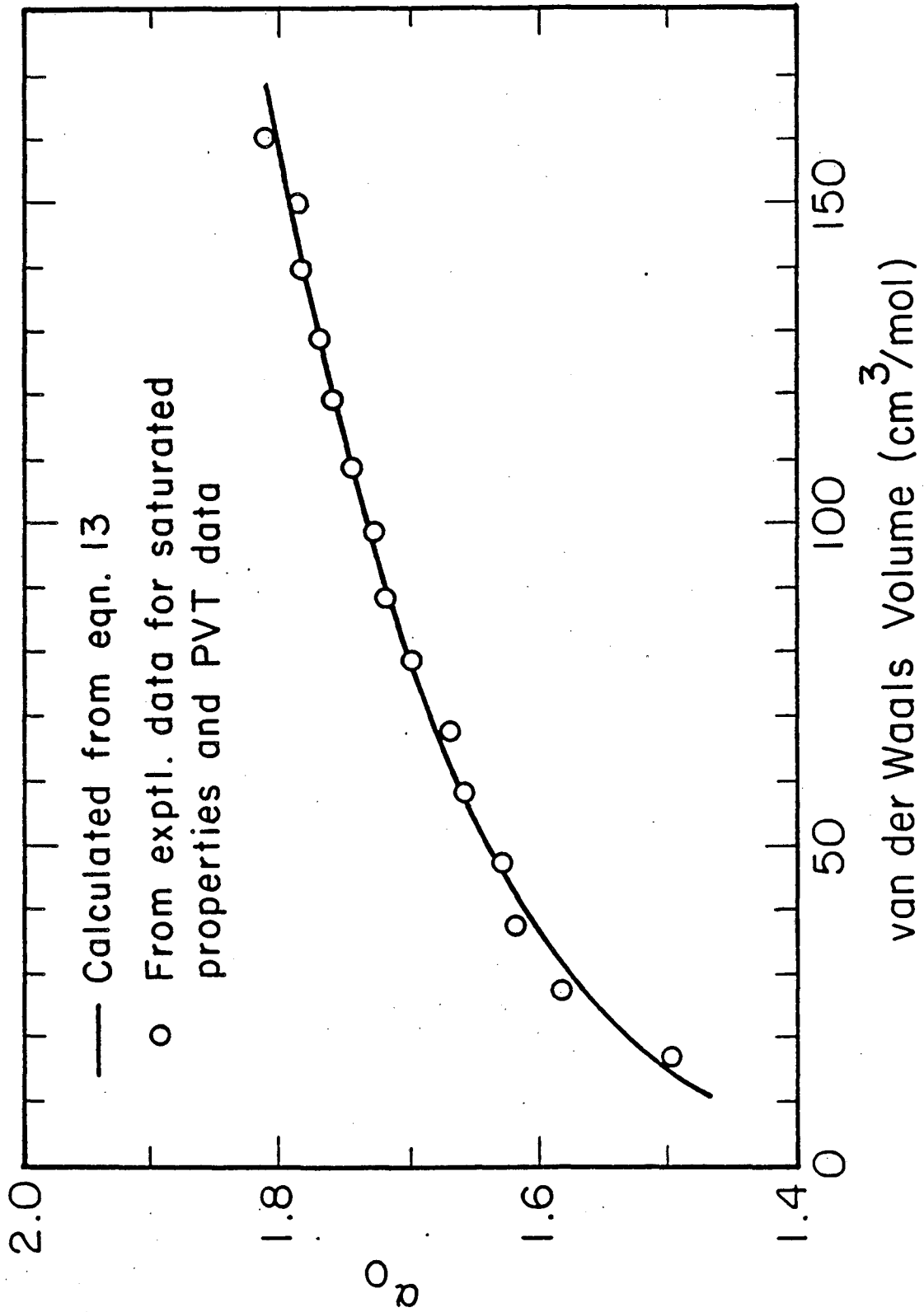Figure 1. Relation between α_0 and V_w for n-alkanes

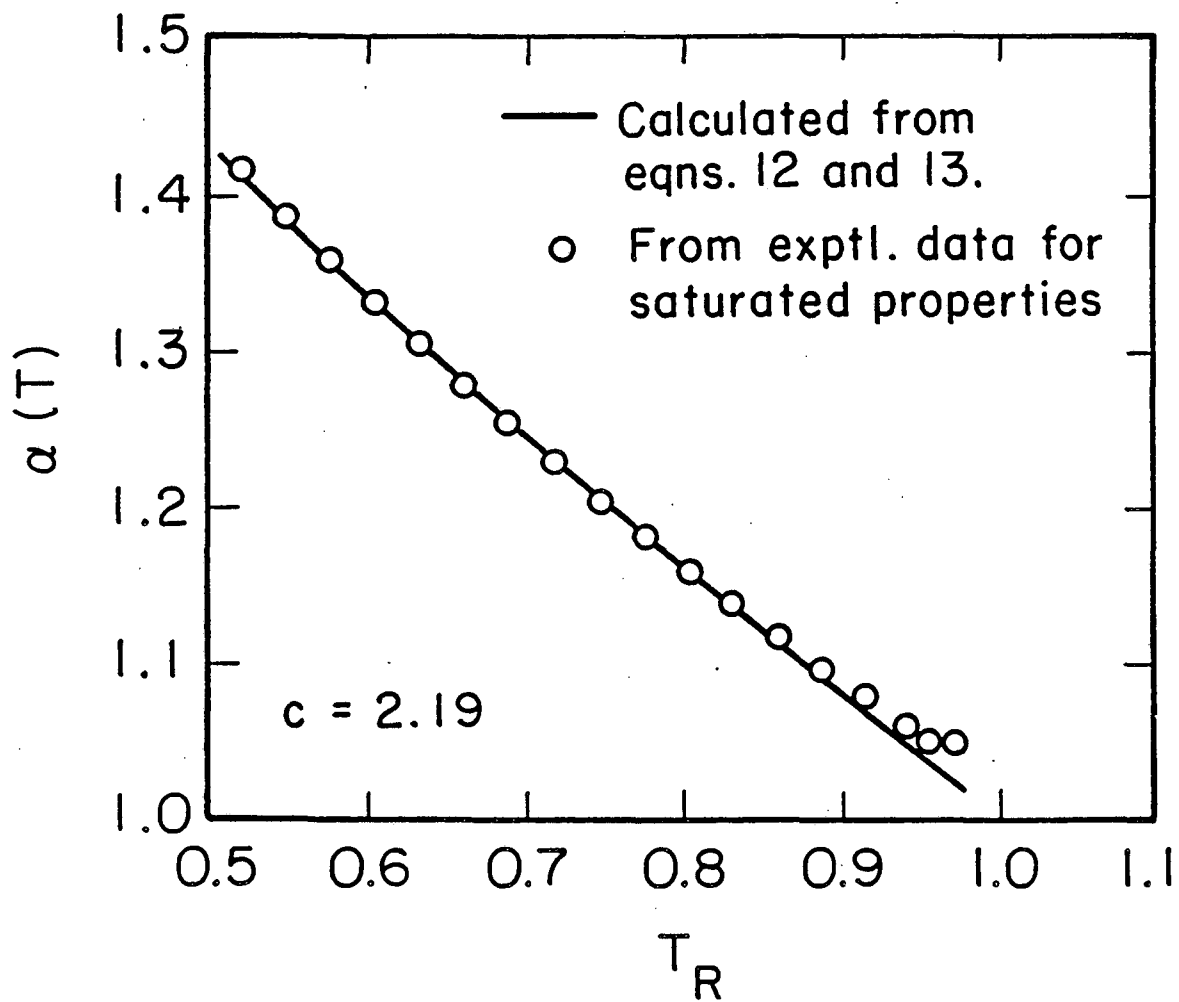Figure 2. Plot of $\alpha(T)$ vs. T_R for n-octane

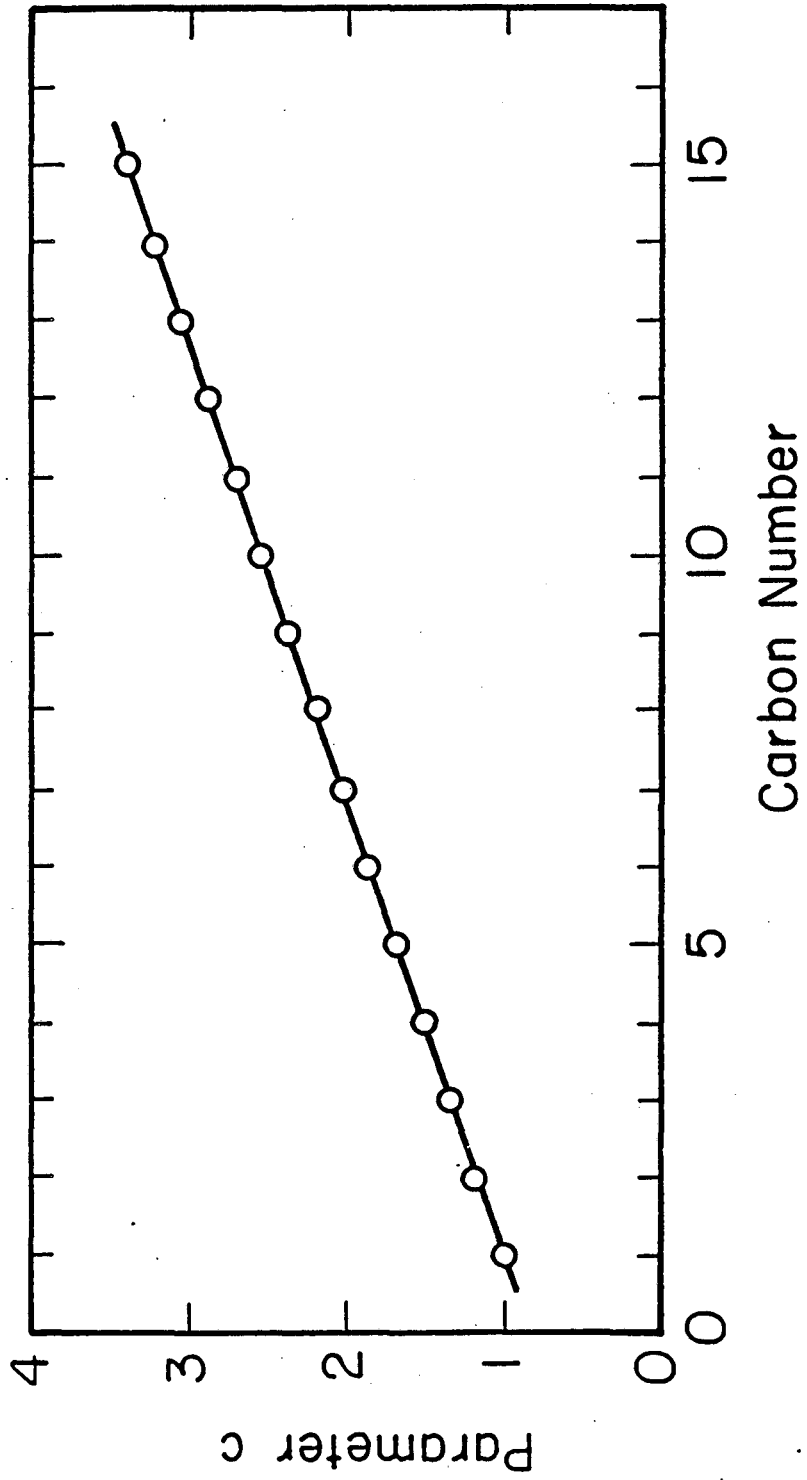Figure 3. Parameter c as a function of carbon number for n-alkanes

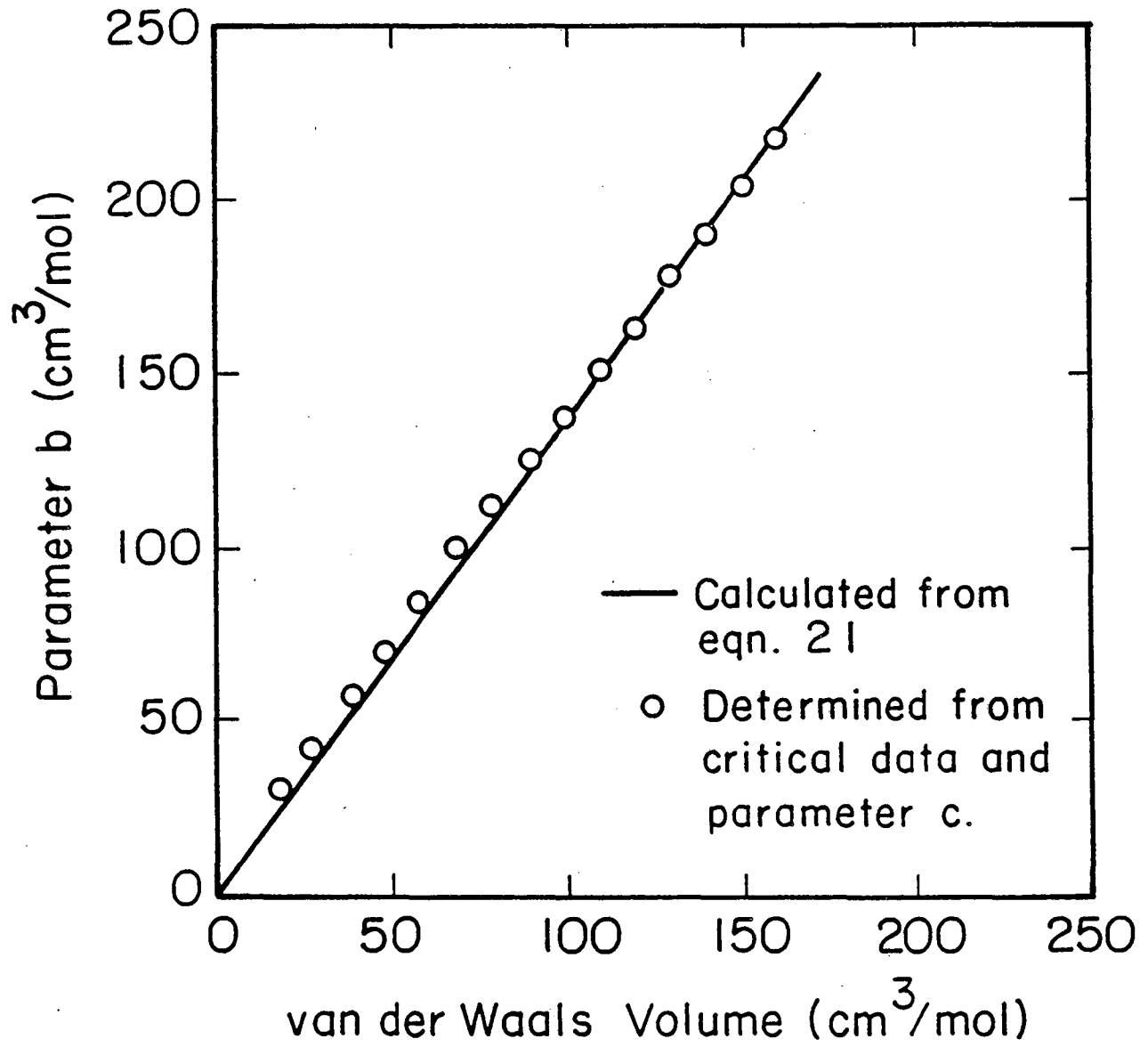Figure 4. Relation between parameter b and V_w

Figure 5. Corresponding-states correlation for temperature-scaling function of parameter a'
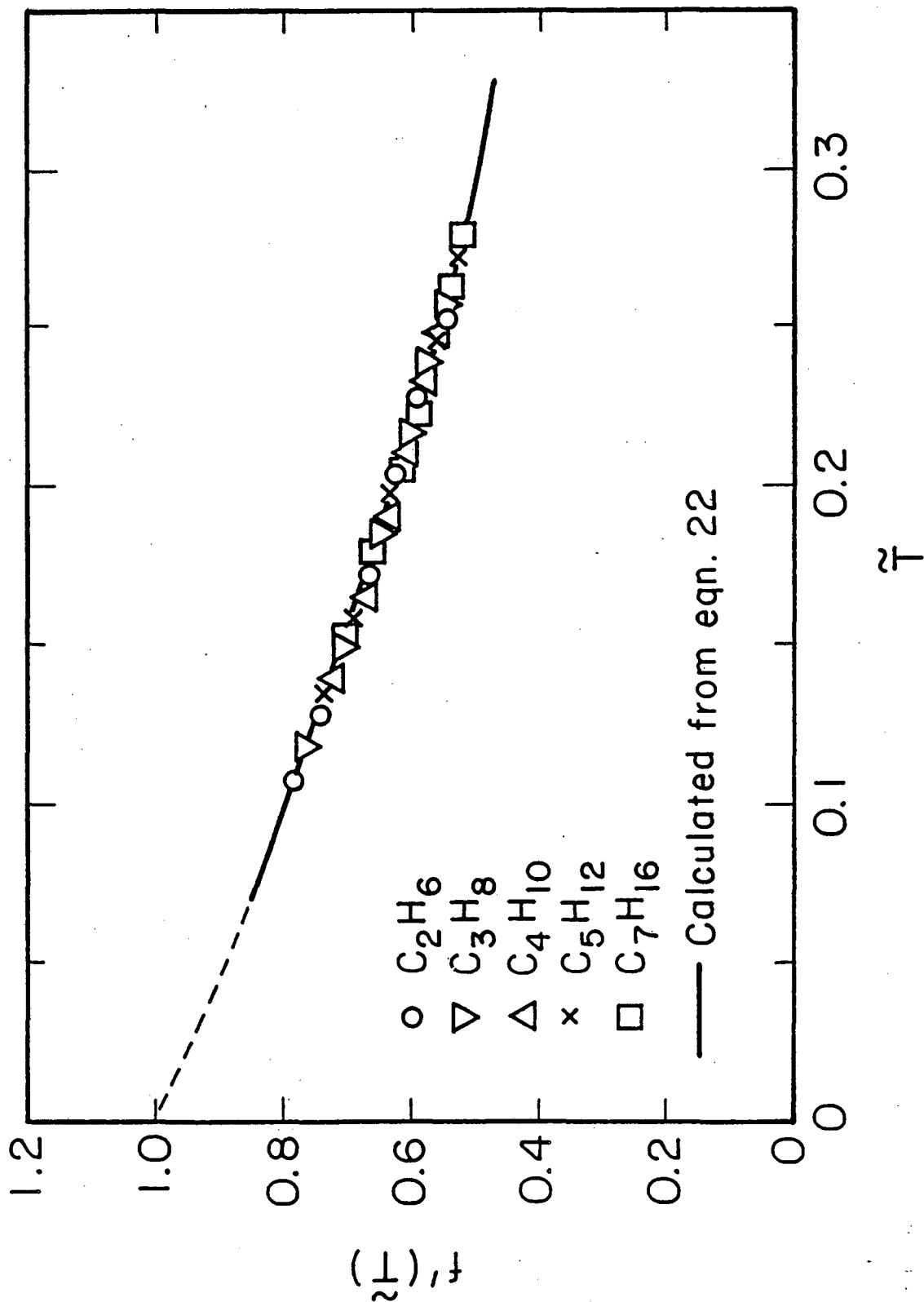
Figure 6. Relation between characteristic potential energy per segment $(cm^3 \cdot bar/mol)$ and chain length for n-alkanes
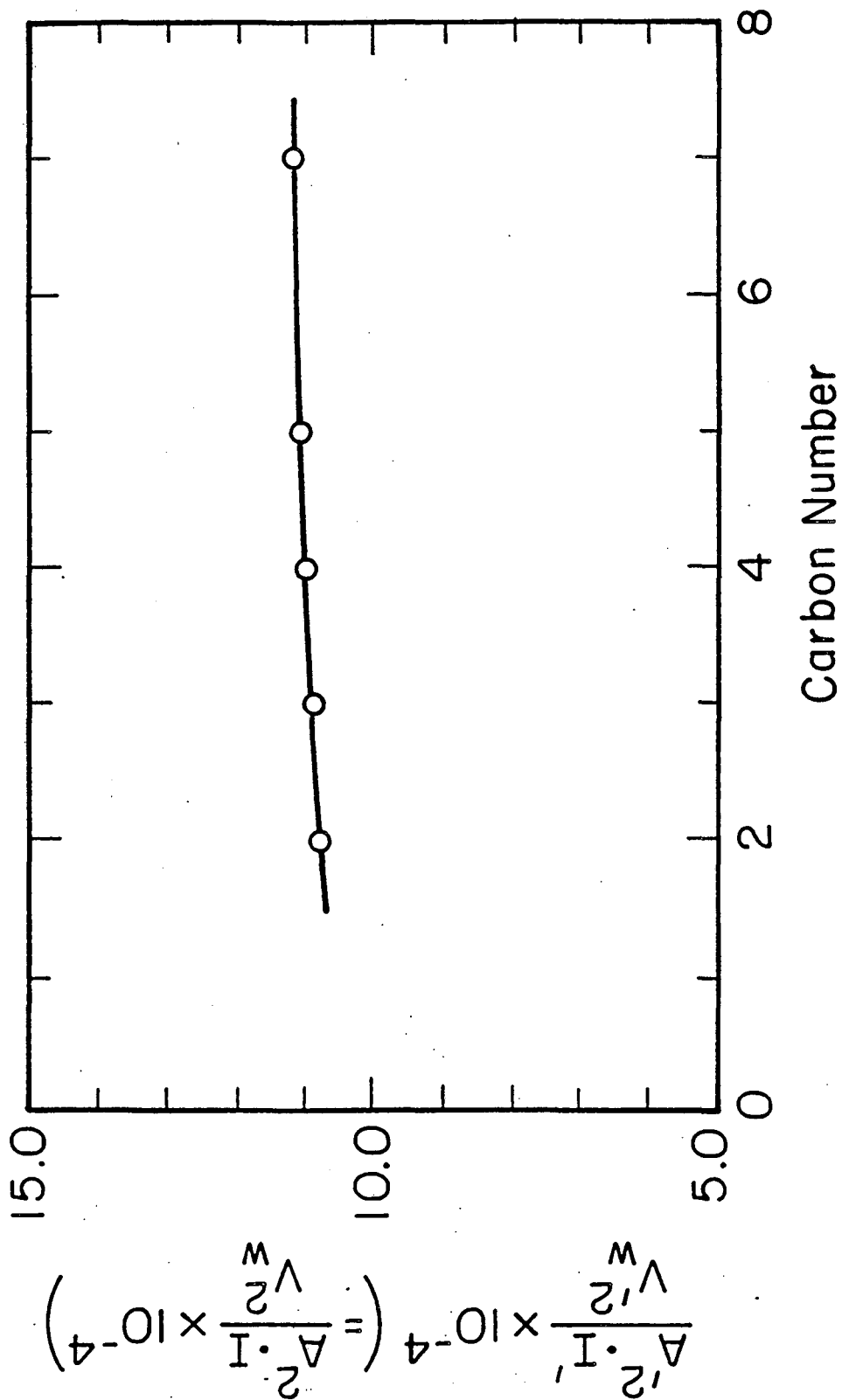
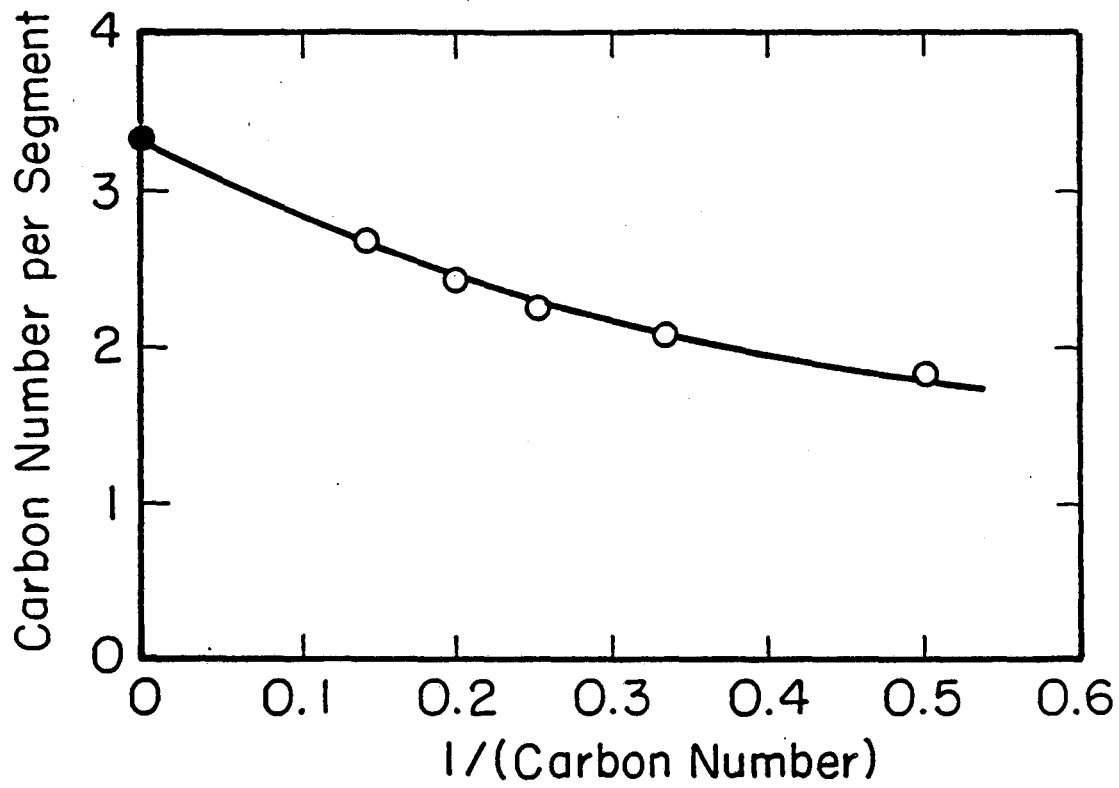Figure 7. Determination of carbon number per segment for polymers

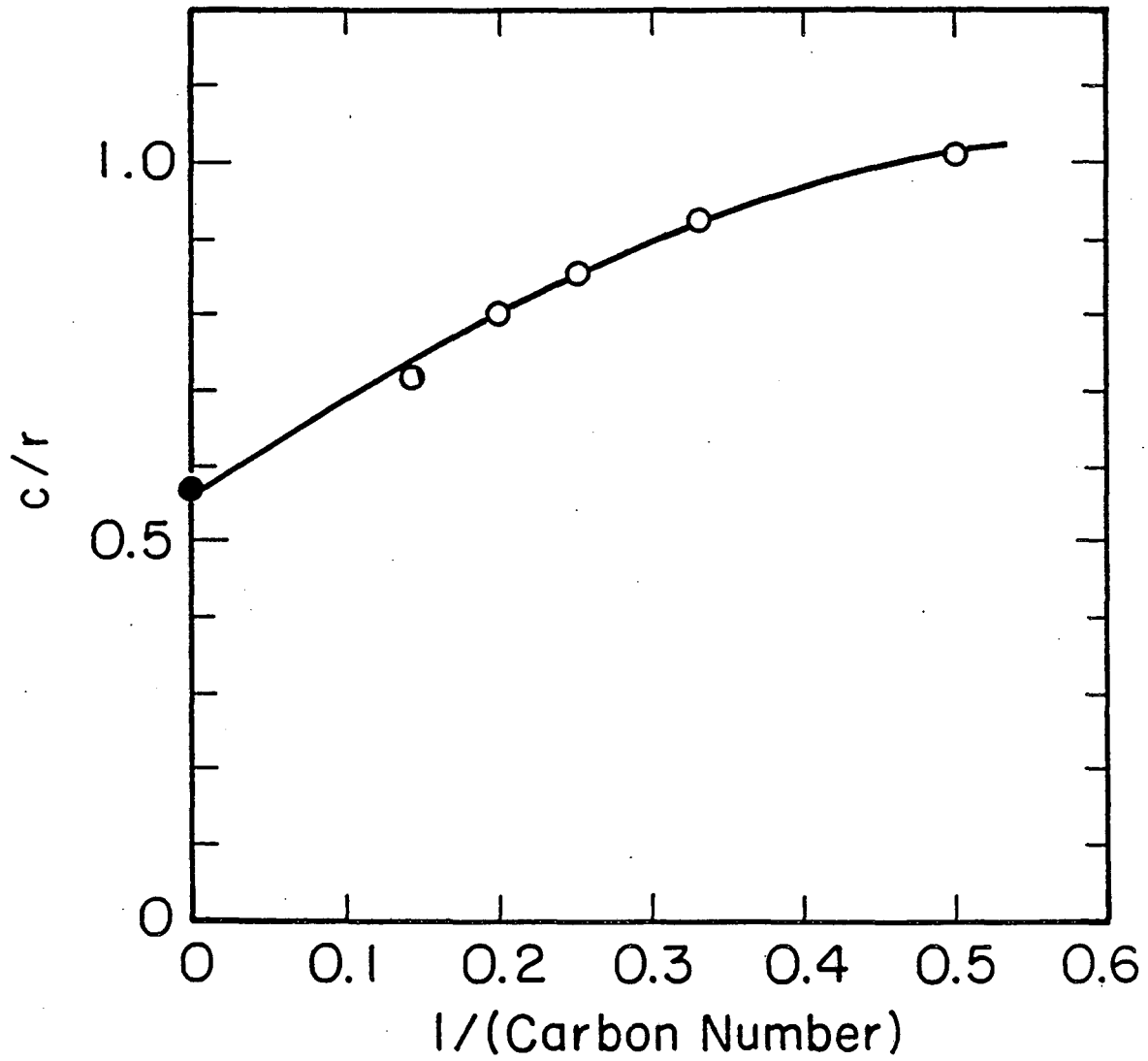Figure 8. Parameter c/r for n-alkanes and polyethylene

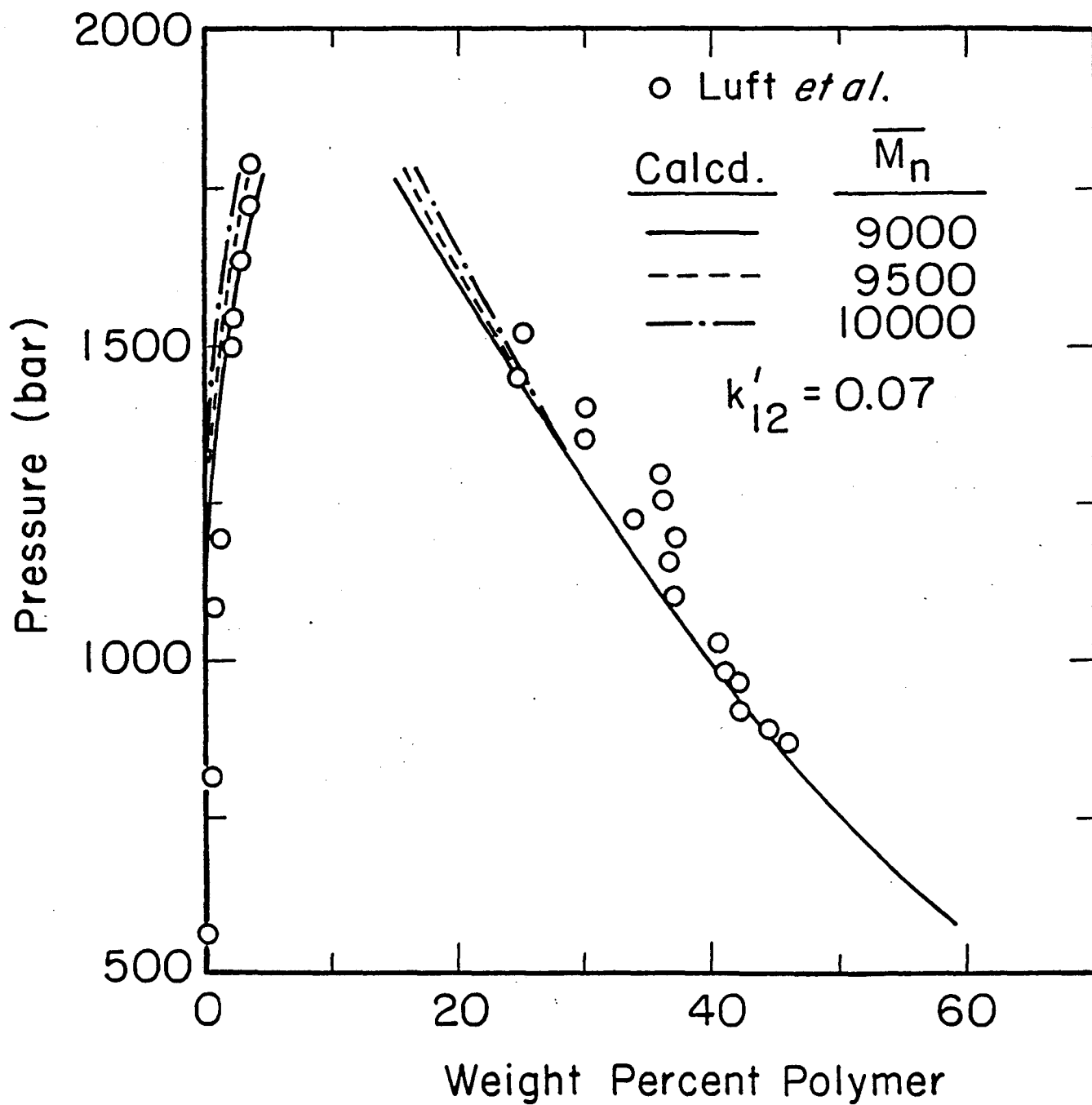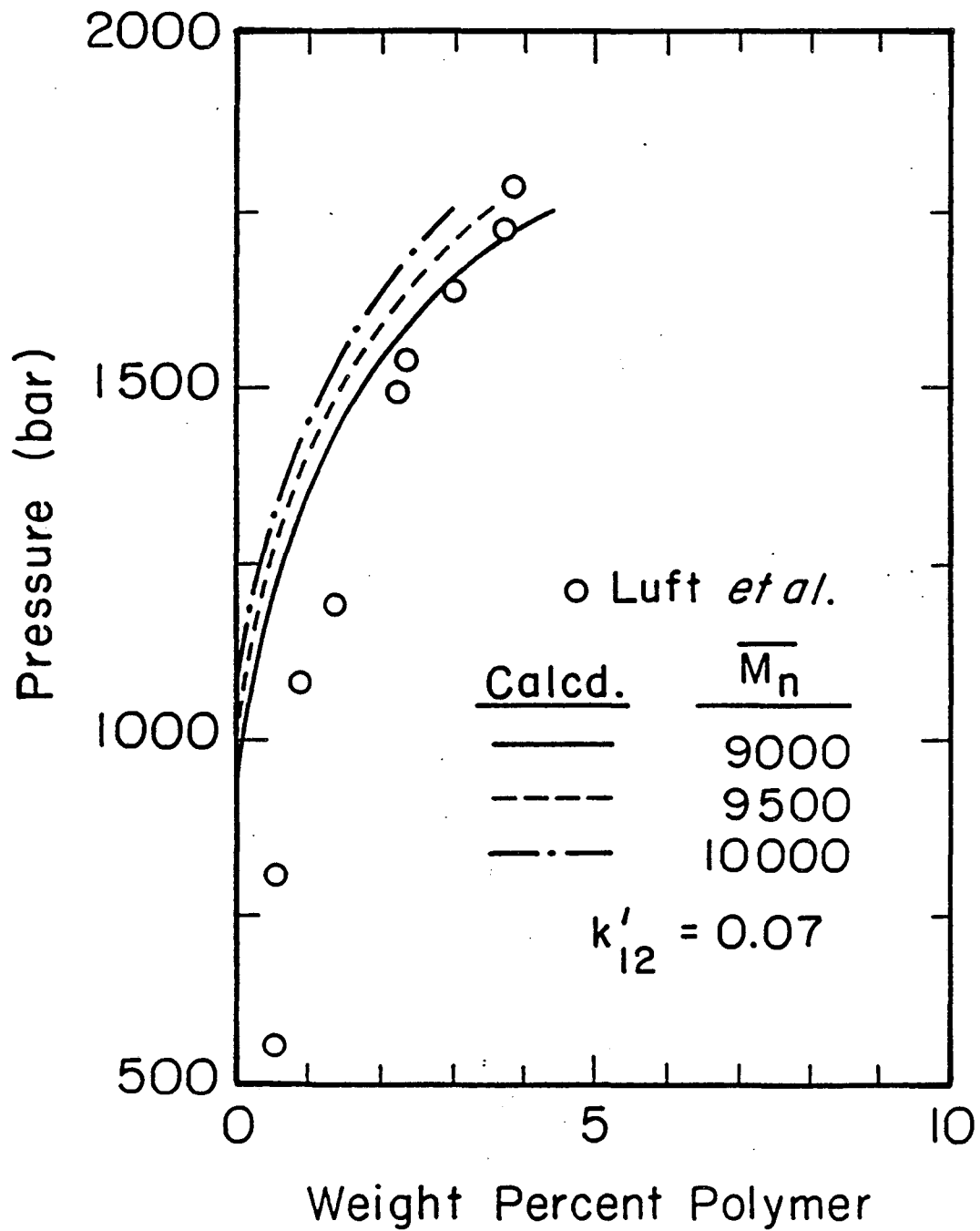Figure 9. Phase diagram for ethylene-polyethylene system at 403.2°K

Figure 10. Solubility of polyethylene in ethylene at 403.2°K

Appendix 1. Potential field E_0 proposed by Soave

From statistical thermodynamics, the partition function for attractive contribution q_a is directly related to the attractive term of an equation of state p_a:

$$\ln q_a = -NE_0/2kT = \int \frac{p_a}{kT}\, dV \tag{A-1}$$

When the attractive term proposed by Soave is used (Soave 1972), we obtain

$$p_a = -\frac{a \cdot N^2}{N_A^2 V^2 + bN_A NV} \tag{A-2}$$

Substitution of Equation (A-2) into Equation (A-1) with the boundary condition $\ln q_a \rightarrow 0$ as $V \rightarrow \infty$, gives

$$\ln q_a = \frac{aN}{kTbN_A} \ln\left(1 + \frac{N}{N_A}\frac{b}{V}\right) \tag{A-3}$$

or

$$E_0 = -\frac{2a}{N_A b} \ln\left(1 + \frac{N}{N_A}\frac{b}{V}\right) \tag{A-4}$$

Appendix 2. Derivation of Equation (18)

If Equation (3) is applied to a close-packed system, we obtain

$$a'^* = -\frac{N_A b'}{2} \cdot \frac{1}{\ln\left(1+\dfrac{Nb'}{N_A V'^*}\right)} \cdot E_0'^*$$

(A-5)

$$= -\frac{N_A b'}{2} \cdot \frac{1}{\ln\left(1+\dfrac{b'}{v'^*}\right)} \cdot E_0'^*$$

where $E_0'^*$ is the potential field experienced by one segment in a close-packed system at volume per segment V'^*. Based on London's formula for the potential energy, we assume that

$$E_0'^* = -\frac{3}{4} A'^2 \cdot I' \cdot z' \cdot s_m' \cdot \frac{1}{d'^6}$$

(A-6)

where d' is the diameter of the segment, z' is the coordination number of the segment, and s_m' is the packing constant. For a face-centered-cubic lattice, $z'=12$, and $s_m'=1.2045$ (Prausnitz el al. 1986b). For a close-packed system, the fraction of space occupied by molecules of diameter d' is (Hansen 1986)

$$\frac{V_w'}{v'^*} = \left(\frac{\pi d'^3}{6}\right) \cdot \left(\frac{\sqrt{2}}{d'^3}\right) = 0.7405 .$$

(A-7)

Van der Waals volume is related to the volume of a spherical segment by

$$\frac{V_w'}{N_A} = \frac{\pi d'^3}{6}$$

(A-8)

If Equation (21) is applied to a close-packed system, we obtain

$$b' = 1.3768 \ V_w'$$

(A-9)

Combining Equations (A-5) - (A-9) with the values for z' and s_m', we obtain

$$a'^* = 2.9108 \cdot \frac{A'^2 \cdot I'}{V_w'}$$

(A-10)

Symbols

A	= polarizability (cm^3/mol)
a	= energy parameter in EOS ($cm^6 \cdot bar/mol^2$)
a_0	= constant in Equation (19)
b	= size parameter in EOS (cm^3/mol)
$3c$	= total number of external degrees of freedom per molecule
D_0	= constant determined from parameter c using Equation (10)
d'	= diameter of segment (cm^3)
E_0	= potential field ($cm^3 \cdot bar/molecule$)
$f'(\tilde{T})$	= dimensionless temperature scaling function of a' in Equations (15) and (19)
I	= first ionization potential ($cm^3 \cdot bar/mol$)
k	= Boltzmann's constant ($cm^3 \cdot bar/molecule \cdot °K$)
k_{ij}	= binary interaction parameter
$\overline{M}_n$	= number-average molecular weight of polymer
N	= number of molecules
N_A	= Avogadro's number
n	= number of moles
p	= pressure (bar)
Q	= canonical partition function
q_a	= partition function for attractive term
$q_{r,v}$	= partition function for rotational and vibrational degrees of freedom
R	= gas constant ($cm^3 \cdot bar/mol \cdot °K$)
r	= segment number per molecule
s_m'	= constant determined from crystal structure
T	= temperature ($°K$)
T_R	= reduced temperature defined by $T_R = T/T_c$
$\tilde{T}$	= reduced temperature defined by Equation (16)
V	= volume ($cm^3/molecule$)
V_f	= free volume ($cm^3/molecule$)
V_w	= van der Waals volume (cm^3/mol)
v	= molar volume (cm^3/mol)
x	= mole fraction in phase α

y	= mole fraction in phase β
z	= compressibility factor
z'	= coordination number of segment
α	= dimensionless temperature-dependent function for parameter a, defined in Equations (11) and (12)
α_0	= parameter defined in Equations (12) and (13)
ε	= characteristic energy ($cm^3 \cdot bar/molecule$)
Λ	= de Broglie wavelength (cm)
ϕ	= fugacity coefficient

subscripts

a	= attractive term of EOS
c	= critical property
ext	= external
int	= internal
i, j	= index of components
m	= mixture
$p.s.$	= segment of polymer
$s.m.s.$	= segment of small molecules such as n-alkanes
$sat.m.$	= saturated monomer

superscripts

α, β	= index of phases
$'$	= segment basis
$*$	= close-packed system

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