On the applicability of the van der Waals potential $E = -\eta/V^m$ to chain molecule liquids

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This paper is dedicated, with great appreciation, to Professor James E. Mark on his 70th birthday.

Abstract

A modified form of the van der Waals expression for the attractive intermolecular potential $E = -\eta/V^m$ has often been used to take account of the acentric character of the potential function, where V is the volume, η a mean-field parameter representing the strength of the interaction field, and m an empirical parameter, usually a constant in the range 1–2. In this article, we have attempted to examine the validity or limitation of this expression in terms of the relevant equation of state terms such as pressure, volume, temperature, and thermal pressure coefficient. The parameters m and η in the equation were estimated separately. A series of n-alkanes including polyethylene, polyoxyethylene, and a segmented dimer compound capable of forming a liquid crystal were investigated. Strictly speaking, the accuracy of the expression was found to be guaranteed only in a limited range of temperature and volume. An interesting behavior was found for m and η in the LC state. Importance of the analysis on anisotropic liquids such as LCs is emphasized.

1. Introduction

The well-known van der Waals equation of state involves two empirical parameters, one for finite size of molecules and the other for attractive forces between the molecules. The concept has been widely adopted in the prescription of the pressure–volume–temperature (PVT) relation of liquids [1]. As Flory pointed out [2], the amazing success of the cell model suggests that the intermolecular repulsions play a dominant role in the liquid. Since molecules are rather closely packed in the liquid state, the cell models are well suited to treatment of the spatial configuration of the system comprising hard cores of finite size. Once the liquid structure has been characterized satisfactorily, one may take account of intermolecular attractions by averaging them over the molecular distribution thus determined.

Prigogine [3] introduced the concept of external degrees

of freedom $3c$ in his treatment of r-mer chain molecules, thus enabling the decoupling of internal and external degrees of freedom for chain molecules. This device was useful in constructing the theoretical framework of the partition function for polymeric liquids [4–11], although the physical significance of the parameter c is not clearly understood. Assuming that the internal degrees of freedom are independent of the environment of the molecule, the configurational partition function can be formulated in terms of the cell partition factor and the mean interaction energy contribution:

$$Z = Z_{\text{ext}}^{3cN} \exp\left(\frac{-E}{kT}\right) \tag{1}$$

Mean-field theories constructed in this manner are shown to be very useful for liquids of simple globular as well as polymeric chain molecules [3–11].

The cell model has often been criticized because of its artificiality: the long-range periodicity involved in the model is apparently incompatible with the short-range order of the real liquid suggested by the radial distribution function. As long as the use of the cell model is limited to

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the appropriate account of configurational arrangements of the elements, the disadvantages arising from its regular periodicity are not so serious as may at first appear. The equation of states derived on this basis are usually free from the geometrical parameters of the model.

The usefulness of the van der Waals expression for attractive interactions has been demonstrated in many examples. After Frank [12], and Hildebrand and Scott [13, 14], the intermolecular interaction potentials such as

$$E = \frac{-\eta}{V^m} \qquad (2)$$

have been widely adopted in conventional mean-field theories of liquids including molten (amorphous) polymers [4–10,15,16]. Here V is the volume, η a mean-field parameter representing the strength of the interaction field, and m an empirical parameter (a constant in the range 1–2) introduced to take account of the acentric character of the potential function. With $m=1$, Eq. (2) reduces to the original van der Waals expression. From the thermodynamic relation,

$$\left(\frac{\delta E}{\delta V}\right)_T = T\gamma - P = \frac{m\eta}{V^{m+1}} \qquad (3)$$

where T is the temperature and γ designates the thermal pressure coefficient,

$$\gamma = \frac{\alpha}{\beta} = \left(\frac{\delta P}{\delta T}\right)_V \qquad (4)$$

Here α is the thermal expansion coefficient and β the isothermal compressibility. The most interesting values of m and η are those corresponding to an atmospheric pressure (i.e. $P \cong 0$). Assuming that η is independent of volume and temperature,

$$\ln T\gamma = -(m+1)\ln V + \ln m\eta \qquad (5)$$

A plot of $\ln T\gamma$ vs. $\ln V$ should give an estimate of m and η, respectively, from the slope and the intercept of the curve. The values of γ can be elucidated from the experimental PVT data reported elsewhere.

In this paper, we wish to report the results of the van der Waals energy analysis outlined above for a series of n-alkanes such as methane (C_1), ethane (C_2), n-undecane(C_{11}), n-tetradecane (C_{14}), n-hexatriacotane (C_{36}) and polyethylene (PE). Polyoxyethylene dimethyl ether (POE) was also investigated because of its unique character of the bond rotation. In view of the increasing importance of thermodynamic studies on chain molecules in the partially ordered state, the results on a dimer compound capable of forming liquid crystal (LC) is also included.

2. Analysis of the thermal pressure coefficient vs. volume relation

The variation of γ with specific volume V_{sp} has been

calculated according to the relation $\gamma = \alpha/\beta$ at given temperatures from the PVT data for C_1 [17,18], C_2 [19, 20], C_{11} [21,22], and PE (MW = 126,000) [21] for the liquid state. In all these nonpolar systems, van der Waals-type intermolecular (intersegmental) interactions prevail. Fig. 1 illustrates the plot of γ vs. V_{sp} for a series of the n-alkanes mentioned above. In each molecular system, the γ–V_{sp} curve tends to shift slightly with temperature. The γ values tend to be enhanced as V_{sp} decreases at given temperatures (i.e. under higher pressures). It is interesting to note that the γ–V_{sp} behaviors are more or less alike for all liquids so that they can be shifted to form a master curve, which reminds us that a simple van der Waals fluid obeys the relation $\gamma = R/(V-b)$, with b being the van der Waals parameter and R gas constant. In this respect, a series of chain molecules examined are not much different from small globular particles in their γ–V_{sp} behaviors, although a quantitative analysis of the correction term b for the finite size is improbable.

3. Estimation of parameters m and η

The $\ln \gamma T$ vs. $\ln V_{sp}$ relation for $P=0$ can be easily derived from Fig. 1. The values of m estimated from these curves according to Eq. (5) are plotted as a function of temperature in Fig. 2. Also included in the figure are the results obtained for C_{14}, C_{36}, and POE (MW = 10^3), the experimental PVT data required being taken from the handbook [21]. In all examples examined, the values of m increase appreciably with temperature. They approach unity (the dotted line) only within a narrow range of temperature. As the molecular weight of n-alkanes increases, the range of the liquid state shifts toward higher temperatures. The m–T curves above C_{11} tend to merge into a group. While the m–T plot of PE tends to intersect the dotted line ($m=1$) at low temperature, the m value of POE remains negative at lower
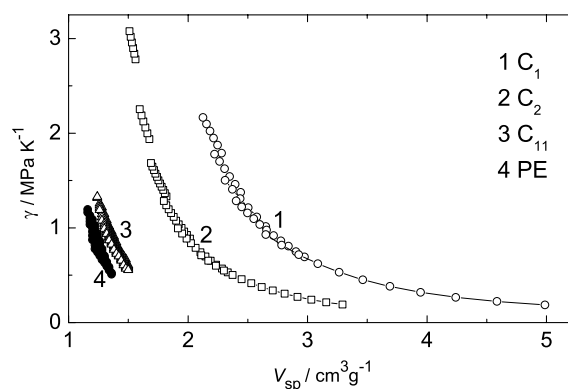

Fig. 1. Plots of thermal pressure coefficient γ vs. specific volume V_{sp} for a series of n-alkanes, estimated by the analysis of PVT data reported in the literature. Calculations were carried out for given temperatures: C_1 [17,18] 100–190 K with 20 K intervals, C_2 [19,20] 100–300 K with 40 K intervals, C_{11} [21,22] 313–493 K with 20 K intervals, and PE [21] 413–533 K with 20 K intervals. For simplicity, details are not indicated in the diagram.
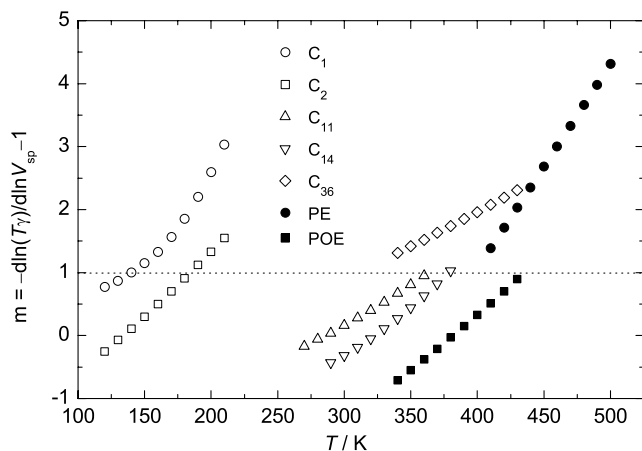
Fig. 2. Variation of m with temperature, estimated according to Eq. (5) for an atmospheric pressure ($P=0$). See the legend to Fig. 1 for C_1, C_2, C_{11}, and PE. The PVT data for C_{14}, C_{36}, and POE were taken from the handbook [21]. The dotted line corresponds to $m=1$.

temperatures and approaches unity at an elevated temperature.

The temperature dependence of η obtained concurrently with m was found to be manifold. The η vs. T plots did not show any reasonable consistency among the compounds examined [23]. Although the physical significance of the two parameters is different, they seem to compensate with each other in the experimental $\ln(T\eta)$ vs. $\ln V_{sp}$ relation. The present attempt to estimate parameters m and η independently from Eq. (5) did not yield any meaningful results, and thus the values of η are not shown here.

In the conventional treatment of liquids, m is often set equal to unity in Eq. (1) [13,14]. The η–T curves derived for $m=1$ are illustrated in Fig. 3. The magnitude of η varies over a wide range from 1000 J cm^3 g^{-2} (C_1) to 420 J cm^3 g^{-2} (POE). The results for C_1 and C_2 are similar to those shown in Rowlinson's book [1] for various small nonpolar molecules such as CH_4, Ar, N_2, and O_2. While C_{11} varies less sensitively with temperature, C_{14}, C_{36}, and PE
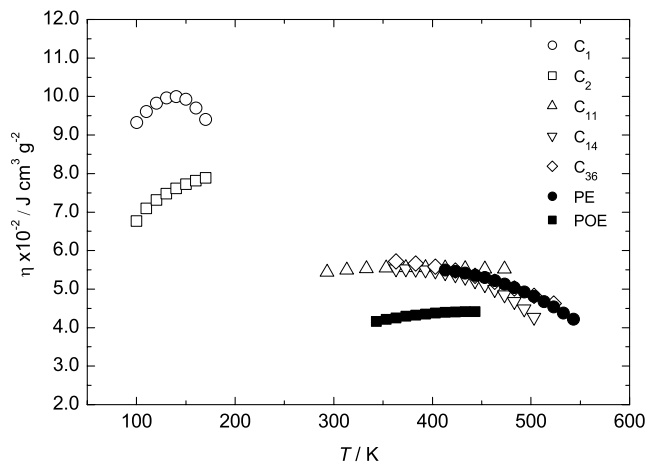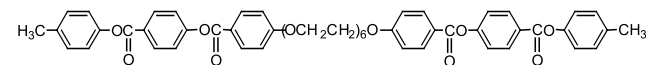

Fig. 3. Variation of η with temperature at zero pressure. Values of η are those estimated by setting $m=1$ in Eq. (5).

exhibit a monotonic decrease with temperature: η goes down from about 550 to 420 J cm^3 g^{-2} ($\sim 30\%$) over the range $T=350$–540 K. For PE, the temperature coefficient d $\ln \eta/dT$ changes from -0.5×10^{-3} K^{-1} (420 K) to -3.6×10^{-3} K^{-1} (540 K).

In contrast to PE, POE exhibits an increase of η with temperature, but the η–T plot tends to level off at higher temperatutes: d $\ln \eta/dT=1.2 \times 10^{-3}$ K^{-1} (340 K)–0 (440 K). POE is known to be one of the most flexible polymers [24] characterized by a small value of the characteristic dimensionless ratio $\langle r^2 \rangle_0/nl^2 \cong 5.0$ as found in various solvents [25–28], where $\langle r^2 \rangle_0$ designates the unperturbed mean-square end-to-end distance of a polymer chain comprising n bonds of length l. A positive temperature coefficient d $\ln \langle r^2 \rangle_0/dT=0.2 \times 10^{-3}$ K^{-1} has been reported from the stress-temperature coefficient of the amorphous sample [29] as well as the viscosity measurement in organic solvents [30]. Somewhat larger values of the mean-square end-to-end distance $\langle r^2 \rangle/nl^2=6.9$ [31] to 5.7 [32] have been reported from the small-angle neutron diffraction analyses on the melt. The dimension was found to decrease gradually with temperature over a wide range, suggesting a small negative temperature coefficient d $\ln \langle r^2 \rangle/dT=-0.3 \times 10^{-3}$ K^{-1} [32] for the melt. In contrast to the *trans*-rich conformation of PE [33], the most preferred arrangement of the POE chain is *gauche* (g^+ and g^-) around the –OC–CO– bond [34–40]. It may be not too surprising to find some difference between these two polymers. Although variations shown cannot be dismissed as experimental error, more experimental studies are needed before drawing any definite conclusion.

4. An extension of the analysis to a dimer compound in the isotropic and nematic LC states

In our laboratory, PVT measurements of a dimer compound named MBBE-6 have been carried out [41,42]. MBBE-6 has two mesogenic units jointed by an oxyethylene-type spacer –(OCH$_2$CH$_2$)$_6$O–, and exhibits an enantiotropic nematic mesophase (N) between the crystal (C) and the isotropic melt (I):

$$\text{H}_3\text{C}\!-\!\!\langle\rangle\!-\!\text{OC}\!-\!\langle\rangle\!-\!\text{OC}\!-\!\langle\rangle\!-\!(\text{OCH}_2\text{CH}_2)_6\text{O}\!-\!\langle\rangle\!-\!\text{CO}\!-\!\langle\rangle\!-\!\text{CO}\!-\!\langle\rangle\!-\!\text{CH}_3$$

C|106.6 °C|N|189.8 °C|I.

The contour length of the spacer (21.4 Å) exceeds those of the hard segments (18.2 Å) jointed on both terminals. The m–T and η–T plots derived according to the same procedure as described above are, respectively, shown in Fig. 4(a) and (b). In MBBE-6, mesogenic cores are more voluminous than the intervening oxyethylene segment. The former part should play a major role in the intermolecular attractive interactions in both isotropic and anisotropic phases. Nevertheless, the trend in the isotropic phase (right-hand side of Fig. 4(a) and (b) resembles those of POE (cf. Figs. 2
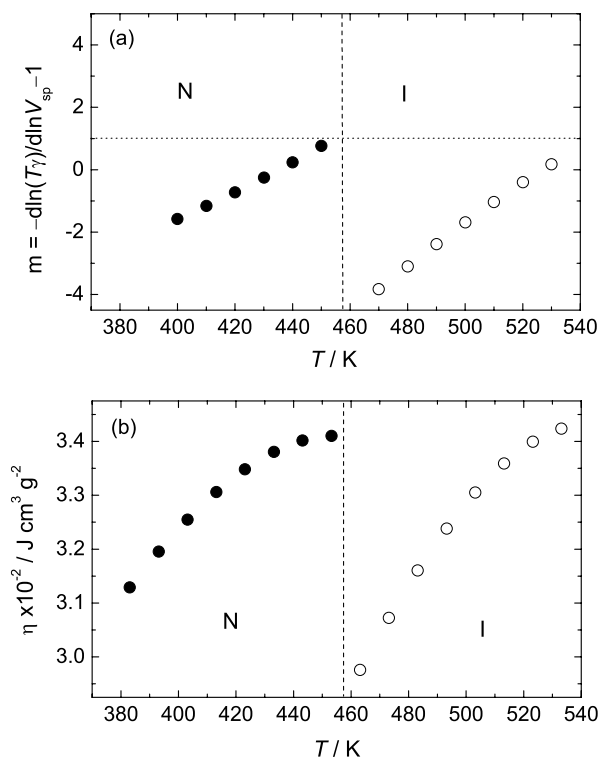
Fig. 4. Variation of (a) m and (b) η as a function of temperature, estimated at zero pressure for MBBE-6 (cf. Eq. (5)). In (a), the dotted line corresponds to $m=1$. Values of η are those estimated by setting $m=1$. The NI phase transition temperature is indicated by the broken lines. The abnormal behaviors observed in the vicinity of the transition point [43–45] are not shown.

and 3). The value of m increases linearly from -3.8 (470 K) to 0.18 (530 K), indicating that the simultaneous elucidation of m and η from Eq. (5) is improbable. The η–T plot estimated for $m=1$ gives a small positive temperature coefficient, $\mathrm{d}\ln\eta/\mathrm{d}T=3.6\times10^{-3}$ K^{-1} (460 K)–0.7×10^{-3} K^{-1} (530 K).

As shown in Fig. 4, both m–T and η–T curves simply shift along the temperature axis by the transition from the isotropic fluid to the LC mesophase, the magnitude of m and η remaining nearly in the same range. To facilitate comparison, the NI transition point is indicated by the broken lines in the figure. The temperature coefficient of the η–T curve ($m=1$) is estimated to be $\mathrm{d}\ln\eta/\mathrm{d}T=2.4\times10^{-3}$ K^{-1} (380 K)–0.3×10^{-3} K^{-1} (450 K). On going from the isotropic to anisotropic LC state, the orientation-dependent attractive interactions come into play [46,47] while the steric interactions (the excluded volume effect) between the mesogenic rods are relaxed [48]. In the LC state, all molecules are required to take an asymmetric shape. Accordingly, chain segments adopt a unique conformer distribution called a nematic conformation [41,42,49–54]. The effect of the conformational transition of the spacer is manifestly demonstrated in an appreciable enhancement of the transition entropy ΔS_{NI} [41,42,49,50] relative to those of the conventional low-molar-mass LCs [55]. The volume

change associated with the NI transition is 0.0042 cm^3 g^{-1}, about 10% of that observed (0.0485 cm^3 g^{-1}) at the CN boundary [42]. In this connection, it might be interesting to note that the α vs. T plot of MBBE-6 exhibits a similar shift between the isotropic liquid and the nematic LC state [42]. As demonstrated in various corresponding state treatment, α is closely related to the free volume ($V-V^*$), with V^* being the core volume of a given molecule [4–10,15,16].

5. Concluding remarks

The present analysis suggests that the empirical equation given by Eq. (2) is valid, strictly speaking, only in a narrow range of volume and temperature. The temperature dependence of m was found to be amazingly large irrespective of the molecular system. From the thermodynamic consistency, adoption of $m=1$ is the most reasonable choice. Since the volume change in the real system is rather small, Eq. (2) is still effective in representing the average intermolecular interaction potential of nonpolar systems. The values of η estimated under this condition ($m=1$) seem to vary depending on the chemical nature of the interacting segment, including the chain length of the molecule. The most interesting difference was observed between the isotropic and nematic LC phase of MBBE-6.

The number of molecules existing at distance $r+\mathrm{d}r$ from the center of a fixed molecule is given as

$$\left(\frac{N}{V}\right)4\pi g(r)r^2\mathrm{d}r \tag{6}$$

where N/V is the number density, and $g(r)$ the radial distribution function representing the characteristic structure of given liquids. As mentioned in the introduction [3–9], a high-density packing of chain molecules may not be so simple as that of small nonpolar molecules. The molecular frequencies of the former consists of two parts, i.e. intra- and inter-molecular modes [3]. The temperature-dependence of the internal and external degrees of freedom should not be the same. Comparison of expressions (2) and (6) immediately suggests that parameter η should be to some extent affected by the local structure of liquids [56,57]. Thermal variation of the local structure could possibly be more pronounced in chain molecule liquids. In this respect, it is interesting to find a common behavior for n-alkanes with sufficient chain length (C$_{11}\sim$PE) (cf. Figs. 2 and 3).

MBBE-6 exhibits somewhat similar behavior with POE, despite of the fact that the contribution from the mesogenic core part [45,46] could be more pronounced in the anisotropic attractive interactions. The nematic conformation is a newly found form of chain molecules [41,42,49–54]. The van der Waals energy analysis described above should yield important information regarding the intermolecular interactions taking place in the anisotropic liquids. Further studies are in progress in our laboratory.

Acknowledgements

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[23] Since $m\eta$ is positive, η is negative for $m < 0$. In the range $\eta > 0$, the η–T plots exhibit an increasing (C_1) as well as decreasing trends (C_2, C_{11}, C_{14}, POE). For C_{36} and PE, the values of η remain nearly invariant with temperature.

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