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An interpretation of molar excess volumes for binary liquid mixtures of cyclohexane with some hydrocarbons using the van der Waals three-fluid mixture equation of state [α]

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Abstract

The simple van der Waals three-fluid mixture equation of state was applied to binary liquid mixtures of cyclohexane with some aromatic hydrocarbons in order to explain the large positive excess molar volume, V^E, of these mixtures. The equation of Carnahan and Starling was selected from among four expressions as an analytical function in the one-fluid equation, because it provided better fitting of the temperature dependence of volumes for the component liquids. Theoretical V^E values were negative if the parameter of attractive force interaction, a_{12}, was defined by the Lorentz–Berthelot rule, but positive if a_{12} was multiplied by an adjustable parameter, ξ, less than unity. This supports the qualitative explanation of the experimental results for such systems. However, the theoretical temperature dependence of V^E did not coincide with the experimental result because of the simplicity of this treatment.

INTRODUCTION

Recently, an apparatus measuring liquid density precisely at various temperatures and pressures was constructed in our laboratory. Using this apparatus, densities of binary mixtures of cyclohexane with some aromatic hydrocarbons were measured at temperatures in the range 298.15–313.15 K, and large positive molar excess volumes V^E were determined from the density data for all the systems [1].

For such binary liquid mixtures consisting of aromatic and aliphatic hydrocarbons, ordinarily large positive V^E values and molar excess enthal-

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pies, H^E, have been reported and qualitatively attributed to the relatively strong intermolecular interaction between aromatic molecules being broken by mixing aromatic with aliphatic compounds, resulting in an unstable mixture and longer average distances between molecules [2,3].

This paper reports a discussion of V^E for these mixtures, using the simple van der Waals three-fluid mixture equation of state, in order to clarify the thermodynamic behavior.

EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus constructed for measuring liquid density at various temperatures consists of a vibrating-tube densimeter cell (DMA-602, Anton Paar, Austria), a thermostatically controlled water bath, a quartz thermometer, a frequency counter and a computer system with various interfaces. The apparatus was calibrated and tested using some standard organic liquids of known density, and the most reliable procedure for precise density determination was established. The accuracy and precision of density measurements were estimated to be less than 1×10^{-5} and 5×10^{-6} g cm^{-3}, respectively.

Density measurements were carried out on binary mixtures of cyclohexane (CH) with benzene (BZ), toluene (TL), ethylbenzene (EB) and heptane (HP) at 298.15, 303.15, 308.15 and 313.15 K. The V^E values for these mixtures were determined from the density data and were found to be large and positive for all the systems. The temperature dependence of V^E was positive for CH–BZ and CH–TL systems but negative for CH–EB and CH–HP systems. Excess thermal expansion coefficients, α^E, for these mixtures were also evaluated from the temperature dependence of V^E. The α^E values were clearly negative except for the CH-rich region in the CH–BZ and the CH–TL systems. The apparatus, experimental procedure and results obtained have been described in detail elsewhere [1].

EQUATION OF STATE AND DISCUSSION

The generalized van der Waals (vdW) equation of state for a one-fluid system having an intermolecular interaction between species i and j is as follows [4]:

$$P_{ij} = (RT/V_{ij})\phi_{ij} - a_{ij}/V_{ij}^2 \tag{1}$$

where R and a_{ij} are the gas constant and a parameter for the average attractive interaction respectively; ϕ_{ij} is an analytical function of the reduced density variable y_{ij} where

$$y_{ij} = b_{ij}/(4V_{ij}) \tag{2}$$

and b_{ij} is a parameter of the core excluding volume.

For ϕ_{ij}, the following four functions were examined

id – vdW: $\phi_{ij} = 1$ (3)

vdW: $\phi_{ij} = 1/(1 - 4y_{ij})$ (4)

CS–vdW: $\phi_{ij} = (1 + y_{ij} + y_{ij}^2 - y_{ij}^3)/(1 - y_{ij})^3$ (5)

1/V4–vdW: $\phi_{ij} = 1 + y_{ij}^3/RT$ (6)

Only eqn. (4), obtained by Carnahan and Starling (CS) [5], is valid for a one-component liquid of hard sphere potential. The last equation (1/V4–vdW) was designed to take account of the Lennard–Jones potential, for which eqn. (1) can be rewritten as

$$P = (RT/V_{ij})\phi_{ij} + (b_{ij}/4)^3/V_{ij}^4 - a_{ij}/V_{ij}^2 \tag{7}$$

Differentiating eqn. (1), the following differential equations were obtained:

$$\frac{1}{\kappa_T} = 2P + \frac{RT}{V}\left[y_{ij}\left(\frac{\partial \phi_{ij}}{\partial y_{ij}}\right)_T - \phi_{ij}\right] \tag{8}$$

$$\frac{1}{\alpha} = \frac{2PV_{ij}}{R\phi_{ij}} - T + \frac{Ty_{ij}}{\phi_{ij}}\left(\frac{\partial \phi_{ij}}{\partial y_{ij}}\right)_P \tag{9}$$

Equation (8) or (9) can be solved numerically with respect to y_{ij} by the Newton–Raphson method using the data for molar volumes, V, and isothermal compressibilities, κ_T, or thermal expansion coefficients, α, at 1 atm and 298.15 K. From these equations, the following relation was obtained for the case $(\partial\phi_{ij}/\partial y_{ij})_T = (\partial\phi_{ij}/\partial y_{ij})_P$:

$$\frac{\alpha}{\kappa_T} = \frac{R}{V_{ij}}\phi_{ij} \tag{10}$$

which is valid except for the 1/V4–vdW equation. Multiplying eqn. (10) by a correction term, ϕ_{ij} was eliminated for the 1/V4–vdW equation, and eventually the expression for α/κ_T agreed with that for the id–vdW equation. The temperature-independent term in eqn. (1), like the second and third terms in eqn. (7), does not affect the expression for α/κ_T.

The comparison of the theoretical α value with the observed one is suitable for determining the functional form of ϕ_{ij}. The various parameters were calculated from y_{ij} obtained by solving eqn. (8) using literature values of κ_T, and then α was calculated for the component liquids by a relationship between α and κ_T as in eqn. (10). The results obtained are listed in Table 1, along with experimental values and the input data. Because the value of α obtained by the CS–vdW equation shows the best agreement with the experimental value, only this type of expression was used in the later calculations for mixtures.

TABLE 1

Observed and theoretical values of thermal expansion coefficients, α, for component liquids calculated using molar volumes, V, and isothermal compressibilities, κ_T, at 1 atm and 298.15 K. The manner of calculated for four equations of state is described in the text

Liquids	V (cm^3 mol^{-1}) Obs.	κ_T (TPa^{-1}) Lit.	α (kK^{-1})			
			Obs.	vdW	CS–vdW	id–vdW 1/V4–vdW
Cyclohexane	108.752	1120 [a]	1.219	0.628	1.274	0.086
Heptane	147.451	1438 [b]	1.251	0.609	1.245	0.081
Benzene	89.410	966 [a]	1.225	0.646	1.300	0.090
Toluene	106.860	906 [a]	1.083	0.562	1.176	0.070
Ethylbenzene	123.086	865 [c]	1.018	0.505	1.091	0.058

[a] Ref. 6.
[b] Ref. 7.
[c] Ref. 8.

Each parameter of the CS–vdW equation obtained for the component liquids is listed in Table 2. As shown in this table, the a_{ij} parameter depends slightly on temperature, through the physical universal constant. On the other hand, y_{ij} and the reduced attractive force parameter, a_{ij}/b_{ij}, of an aromatic hydrocarbon are not as large as those for an aliphatic hydrocarbon. These points need further investigation in the one-fluid equation of state.

There are three methods for combining the van der Waals equation of pure component liquids into the equation for its mixture, i.e. one-fluid (vdW-1), two-fluid (vdW-2) and three-fluid (vdW-3) mixture equations of state [9]. Of these equations, vdW-1 has already been investigated by Kumaran et al. [10], and it has most probably been used because of its simplicity and good correlation with the observed state. However, we adopted the vdW-3 equation because of its rather clear physical meaning based on the cell model theory.

TABLE 2

Parameters of CS–vdW equation of state estimated for component liquid at 1 atm and 298.15 K. The a_{ii} values in parentheses were calculated from the b_{ii} parameter fixed at 298.15 K and molar volume observed at 313.15 K

Liquids	b_{ii} (cm^3 mol^{-1})	$a_{ii} \times 10^{-7}$ (atm cm^6 mol^{-2})	$a_{ii} \times 10^{-5}/b_{ii}$ (atm cm^3 mol^{-1})	y_{ii}
Cyclohexane	226.04	3.9572 (3.9621)	1.7507	0.51961
Heptane	309.15	5.5387 (5.5320)	1.7916	0.52416
Benzene	184.40	3.1640 (3.1710)	1.7158	0.51561
Toluene	229.02	4.3609 (4.3752)	1.9042	0.53579
Ethylbenzene	271.39	5.6210 (5.6348)	2.0712	0.55122

For a random mixture, the equation of state for vdW-3 was defined as follows:

$$P = x_1^2 P_{11} + 2x_1 x_2 P_{12} + x_2^2 P_{22} \tag{11}$$

where P_{ij} is the partial pressure caused by the interaction between i and j species, calculated from eqn. (1). Parameters a_{12} and b_{12} were evaluated on the basis of the modified Lorentz–Berthelot rule [11,12] as follows:

$$a_{12} = \xi b_{12}\left[a_{11}a_{22}/(b_{11}b_{22})\right]^{1/2} \tag{12}$$

$$b_{12} = \left[\left(b_{11}^{1/3} + b_{22}^{1/3}\right)/2\right]^3 \tag{13}$$

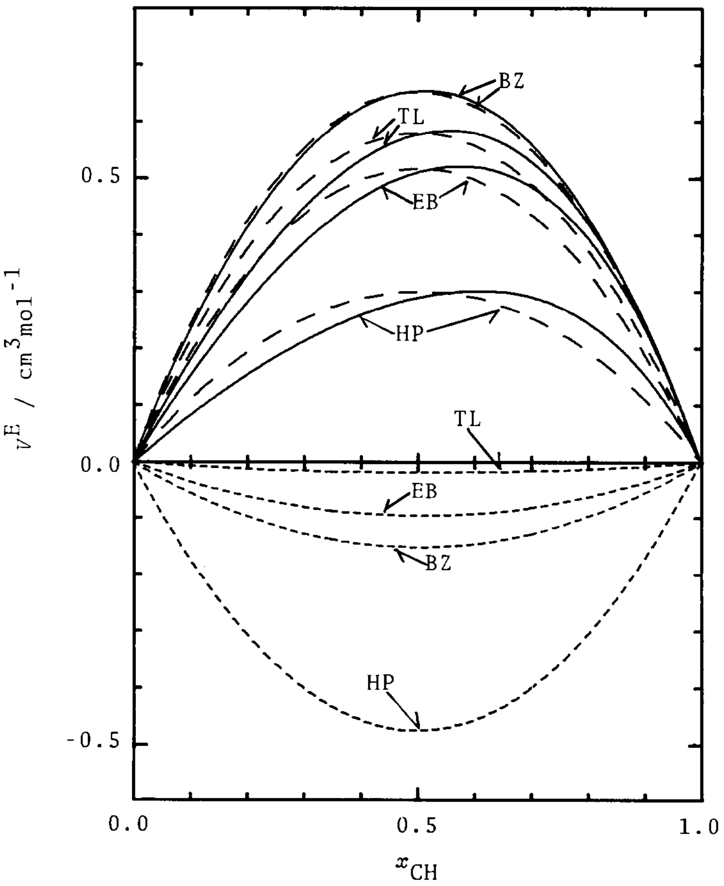

Fig. 1. Molar excess volume, V^E, of the binary liquid systems of cyclohexane (CH) with benzene (BZ), toluene (TL), ethylbenzene (EB) and heptane (HP) at 1 atm and 298.15 K. Solid lines are experimental results; broken and dotted lines are theoretical values calculated using the vdW-3 mixture equation of state at $\xi = 1$ and at optimized ξ respectively.

where ξ is an adjustable parameter. Molar cell volumes, V_{ij}, were defined using partial molar volumes, V_i, as follows:

$$V_{ii} = V_i$$

$$V_{12} = (V_1 + V_2)/2 \qquad (14)$$

In addition, to determine two unknown variables easily, we assumed that the pressure acting on each molecule in a cell is equal to the total pressure. Consequently V^E could be calculated from V_1 and V_2, which were obtained by solving the following simultaneous equations:

$$P = x_1P_{11} + x_2P_{12} = x_1P_{12} + x_2P_{22} \qquad (15)$$

Calculation was carried out by the simultaneous Newton–Raphson method, and the results obtained are shown in Fig. 1, along with the experimental curves.

As shown in Fig. 1, theoretical V^E values were negative for all systems with $\xi = 1$, but the sequence in value was in agreement with the experimental results. The negative V^E values at $\xi = 1$ are considered to be essential to a mixture composed of spherical molecules differing in size and attractive

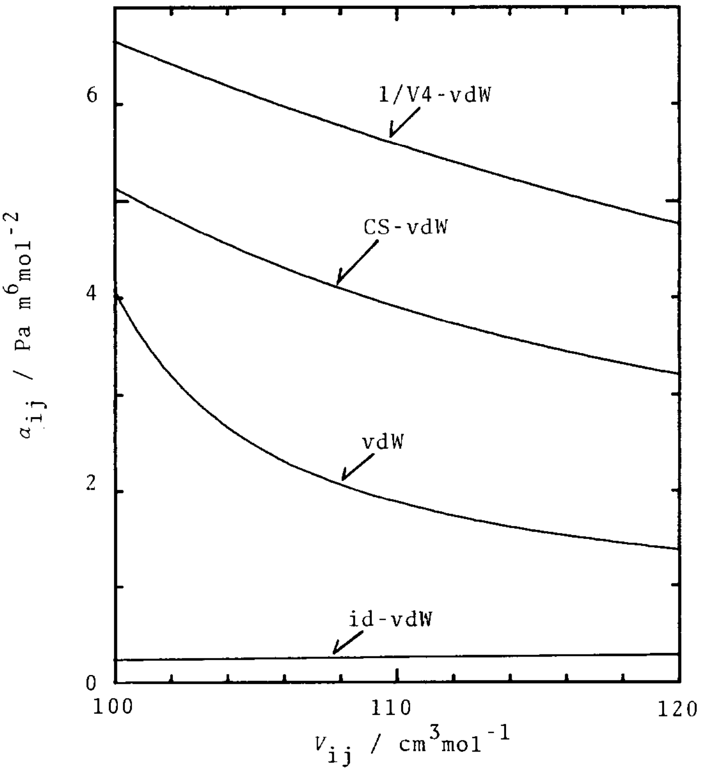

Fig. 2. Volume dependence of a_{ij} parameter for four one-fluid equations of state calculated at 1 atm and 298.15 K. The b_{ij} parameter was fixed at the value estimated for benzene.

force, and further support derives from the volume dependence of the a_{ij} parameter for the one-fluid equation of state. The curves in Fig. 2 are concave except for that of the id–vdW expression, and a_{12} at $\xi = 1$ calculated by eqn. (12) has almost the same value as the arithmetic mean of a_{11} and a_{22}, so the value of $V_{12}(a_{12})$ is obviously less than the arithmetic means of $V_{11}(a_{11})$ and $V_{22}(a_{22})$. Thus the ξ parameter is always below unity for systems which show positive V^{E} values.

Positive values of V^{E} were found at the following ξ values: 0.959 (CH–BZ), 0.970 (CH–TL), 0.970 (CH–EB) and 0.968 (CH–HP). A value of $\xi < 1$ for mixtures composed of aliphatic and aromatic hydrocarbons means that the attractive interaction between different molecules is relatively weak, and supports the qualitative explanation described above. This tendency is remarkable for the CH–BZ mixture.

The concentration dependence of theoretical V^{E} values did not, however, coincide with the experimental results, and a similar result of $\xi < 1$ was also

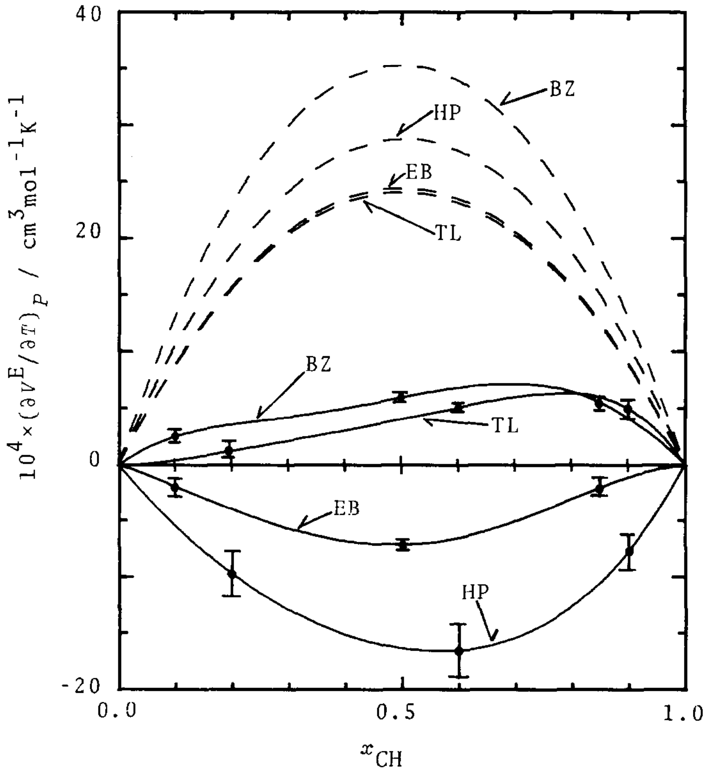

Fig. 3. Temperature dependence of molar excess volume, $(\partial V^{\mathrm{E}}/\partial T)_p$, the binary liquid systems of cyclohexane (CH) with benzene (BZ), toluene (TL), ethylbenzene (EB) and heptane (HP) at 1 atm between 298.15 and 313.15 K. Solid lines and error bars are experimental results and standard errors [1], respectively; broken lines are theoretical values calculated using the vdW-3 mixture equation of state with the optimized value of ξ.

found for the CH–HP mixture. The positive V^E of this system may be considered to arise from the loose packing due to differences in molecular shape of the component liquids. The findings reflect the simple nature of this treatment. In particular, these equations of state do not reflect at all the effect of molecular shape and local concentration fluctuation.

The theoretical temperature dependence of V^E was also calculated using the optimized ξ parameter. Results obtained are shown in Fig. 3, along with experimental results. Theoretical values are fairly large and positive for all the systems, and the sequence is not in agreement with that observed. This suggests that the model for this treatment is too simple to explain the temperature or pressure dependence of V^E. Tokiwano and Arakawa calculated the interaction energy parameters a_{12} and excess thermodynamic functions for some binary liquid mixtures more rigorously on the basis of statistical thermodynamics [13]. We are interested in the interpretation of the temperature and pressure dependence of V^E for these mixtures by applying their treatment.

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