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PVT Relationships of Binary Mixtures of Indole with 2-Methylnaphthalene and Biphenyl at 333.15 K and Pressures up to 270 MPa

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Abstract *PVT* relationships of two binary mixtures of indole with 2-methylnaphthalene and with biphenyl have been measured at 333.15 K and at pressures up to 270 MPa or up to near the freezing pressure of each mixture. The compositions in mole fraction of indole were set to be 0.2500, 0.5000, and 0.7500 for both systems. *PVT* relationships of indole (at 343.15 K and 353.15 K), 2-methylnaphthane (at 333.15 K and 343.15 K), and biphenyl (at 353.15 K and 363.15 K) under pressure and those for the binary mixtures at 0.1 MPa in the temperature range from 293.15 K to 363.15 K were also measured. *PVT* data were analyzed with the use of the Tait equation and Carnahan–Starling–van der Waals (CS–vdW) equation. It was found that both the equations can be used to represent the experimental *PVT* relationships for the pure compounds and the binary mixtures with an average absolute deviations of 0.04 % for the Tait equation and 0.29 % for the CS–vdW equation. As for mixture density calculations with the CS–vdW equation, the effect of mixing rules was investigated.

Keywords Binary mixture · Biphenyl · Density · Equation of state · Excess volume · High pressure · Indole · 2-Methylnaphthalene · *PVT* relationships

1 Introduction

PVT relationships of liquid mixtures under pressure are essential for the correlation of transport properties, ultrasonic speeds of sound, and related thermophysical properties [1–4] and also for the design of a high-pressure crystallization process developed by Moritoki et al. [5,6]. We have been trying to develop an indole recovery process

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from wash oil fractions of coal tar liquids by the high-pressure crystallization method [7–9]. To determine an optimum operation condition, we needed an accurate predictive method for the high-pressure solid–liquid equilibria for the mixture containing indole.

With respect to the high-pressure crystallization process, we reported the melting temperature of several polycyclic and heterocyclic aromatic compounds under pressure [10,11], high-pressure solid–liquid equilibria of indole-1-methylnaphthalene mixtures [12], and solid–liquid equilibria of binary mixtures containing indole at 0.1 MPa [13]. We explored a predictive method for high-pressure solid-liquid equilibria of the simple eutectic systems based on an equation of state [12,14]. Good agreement between the experimental results and predictions were observed for the case when an accurate equation of state for liquid mixtures and solid densities of pure compounds were available. To ascertain the usability of this predictive method, reliable experimental data were required for the solid–liquid equilibria and *PVT* relationships for the mixture containing indole and other major components in the wash oil fractions of coal liquids, such as naphthalenes, biphenyls, and quinolines.

As a continuing study for the development of the high-pressure crystallization process, in this study we measured *PVT* relationships of the binary mixtures of indole with 2-methylnaphthalene and with biphenyl at 333.15 K and at pressures up to 270 MPa or up to near the freezing pressure of each mixture. In order to correlate the experimental data with equations of state, we also measured the *PVT* relationships of the two binary mixtures at 0.1 MPa in the temperature range from 293.15 K to 363.15 K and those of pure indole, 2-methylnaphthalene, and biphenyl in the temperature range from 313.15 K to 353.15 K and at pressures up to 140 MPa or up to near the freezing pressure.

The *PVT* relationships were correlated with the Tait equation and the CS–vdW equation of state. In calculations with the CS–vdW equation, the effect of mixing rules for the equation-of-state parameters on the molar volume calculation was investigated. The excess molar volumes at 0.1 MPa were analyzed with an empirical Redlich–Kister type V^{E} equation. The excess molar volumes under pressure were calculated with the CS–vdW equation of state.

2 Experimental

The specific volume was measured with a glass piezometer. Details of the piezometer and experimental procedures were described previously [15–17]. The temperature of the thermostat was observed with a quartz thermometer calibrated against a Leeds–Northrup platinum resistance thermometer. The pressure was observed with a Heise Bourdon gauge calibrated against a dead-weight tester. Mixtures were prepared by weighing the liquids. A Sartorius balance having a stated precision of 0.1 mg was used for weighing. The maximum estimated uncertainties of temperature and pressure were, respectively, 0.01 K and 0.05 MPa up to 100 MPa and 0.12 MPa in the range from 100 MPa to 270 MPa. The minimum possible uncertainty in the mole fraction determination is estimated to be 0.0001. The mean error in measurements of volume was no greater than $\pm 0.0001\ \mathrm{cm}^3 \cdot \mathrm{g}^{-1}$.

Indole, 2-methylnaphthalene, and biphenyl were obtained from Aldrich Chemical Co. Inc. and benzene was from Wako Pure Chemical Ind. Ltd. The purities certified by the manufacturers were as follows: indole—99.0 %, 2-methylnaphthalene—98.0 %, biphenyl—98.0 %, and benzene—99.8 %. We checked the purities of the samples by gas chromatography and found that the purities were as follows: indole—99.8 mol %, 2-methylnaphthalene—9.8 mol %, biphenyl—99.9 mol %, and benzene—99.9 mol %. Benzene was dried by treating for a long period over predried 5 Å molecular sieves, while indole, 2-methylnaphthalene, and biphenyl were used without further purification.

3 Results

To check our experimental procedures, we measured the liquid densities of benzene as a standard substance. Table 1 shows comparisons of the measured values of benzene with corresponding literature values [18–21]. We also show the same comparisons for 2-methylnaphthalene [22–24]. Specific volumes of indole and biphenyl have not been previously reported. As can be seen, the present results show reasonably good agreement with literature values for benzene. As for 2-methylnaphthalene, the present results deviate about 0.06 % to 0.63 % from literature values [22,23]. The present results, however, show reasonably good agreement with interpolated values from the data obtained by Hales and Townsend [24]. Since we measured the specific volumes of water under pressure with the same experimental apparatus and methods in our previous study [15] and obtained reasonably good agreement with literature values, it should be reasonable to consider that the present specific volume data under pressure are reliable.

Tables 2 and 3 present specific volumes of the indole + 2-methylnaphthalene and indole + biphenyl systems under pressure, respectively. Figures 1 and 2 show the experimental results for the two systems. Table 4 shows the experimental specific volumes under pressure for indole, 2-methylnaphthalene, and biphenyl. The specific volume of indole at 333.15 K was reported in our previous study [12]. Tables 5 and 6 list the experimental results at 0.1 MPa for the indole + 2-methylnaphthalene and indole + biphenyl systems, respectively. It should be mentioned that the specific volume of biphenyl at 333.15 K was measured under supercooled conditions.

4 Correlations

4.1 Excess Molar Volume at 0.1 MPa

The excess molar volume V^{E} was obtained from the experimental molar volume at 0.1 MPa for the two mixtures with the following equation,

$$V^{\mathrm{E}} = (x_1 M_1 + x_2 M_2)V - (x_1 M_1 V_1 + x_2 M_2 V_2) \tag{1}$$

where V is the specific volume of the mixture, and V_i, M_i, and x_i are the specific volume, molar mass, and mole fraction, respectively, of pure component i ($i = 1, 2$;

Table 1 Comparison of the specific volumes of benzene and 2-methylnaphthalene with literature results

Substance	T (K)	Specific volume ($\mathrm{cm^3 \cdot g^{-1}}$)	References
Benzene	293.15	1.13769	[14]
	293.15	1.13766	[15]
	293.15	1.13766	[16]
	293.15	1.13770	[17]
	293.15	1.1377	This study
2-Methylnaphthalene	313.15	1.00964	[18]
	313.15	1.0039	[19]
	310.00	1.00663	[20]
	313.15	1.00909	[20][a]
	333.15	1.02491	[20][a]
	353.15	1.04130	[20][a]
	313.15	1.0088	This study
	333.14	1.0247	This study
	353.15	1.0406	This study

[a] Interpolated values

1: indole, are 2: 2-methylnaphthalene or biphenyl). The values of V^{E} at 353.15 K are plotted against the mole fraction of indole in Fig. 3. It can be seen that the values of V^{E} show negative deviations over the entire composition range with maxima at around $x_1 = 0.5$ for both the systems. The absolute values of V^{E} for the indole + biphenyl system are about a factor of two larger than those for the indole + 2-methylnaphthalene system.

The excess molar volumes were correlated with the following Redlish–Kister type equation:

$$V^{\mathrm{E}} = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{2}$$

where a_i's ($i = 0, 1, 2$) are the fitting parameters. For both the systems, the values of these parameters, a_i ($i = 0, 1, 2$), are determined. The values of a_i and deviations of the calculated values from the experimental results are listed in Table 7. The solid lines in Fig. 3 represent the calculated values from Eq. 2.

4.2 Densities Under Pressure

Liquid volumes under pressure can be represented with the Tait equation with high accuracy. We fitted the present experimental results with the Tait equation expressed as follows:

$$(V_0 - V)/V = C \ln[(B + P)/(B + P_0)] \tag{3}$$

where V and V_0 are the specific volume at the corresponding pressures, P and a reference pressure P_0, respectively, and B and C are fitting parameters. In this study,

Table 2 Specific volumes of indole + 2-methylnaphthalene system under pressure at 333.15 K

	Specific volume ($cm^3 \cdot g^{-1}$)				
	Mole fraction of indole				
P (MPa)	0.0000	0.2500	0.5000	0.7500	1.0000
0.1	1.0247	1.0048	0.9836	0.9609	0.9360
10.0	1.0183	0.9988	0.9782	0.9560	0.9315
20.0	1.0123	0.9930	0.9730	0.9513	0.9273
30.0	1.0069	0.9876	0.9679	0.9467	0.9228
40.0	1.0013	0.9824	0.9633	0.9422	0.9192
50.0	0.9961	0.9776	0.9586	0.9379	0.9157
60.0	0.9915	0.9732	0.9544	0.9341	
70.0	0.9868	0.9685	0.9504	0.9304	
80.0	0.9826	0.9645	0.9464	0.9267	
90.0	0.9784	0.9607	0.9427	0.9233	
100.0	0.9749	0.9569	0.9391	0.9198	
110.0		0.9533	0.9358	0.9167	
120.0		0.9497	0.9325	0.9134	
130.0		0.9464	0.9292	0.9104	
140.0		0.9432	0.9262	0.9077	
150.0		0.9400	0.9231	0.9048	
160.0		0.9369	0.9202	0.9020	
170.0		0.9340	0.9174		
180.0			0.9148		
190.0			0.9122		
200.0			0.9095		
210.0			0.9070		
220.0			0.9047		
230.0			0.9023		
240.0			0.8999		
250.0			0.8977		
260.0			0.8956		
270.0			0.8934		

the reference pressure P_0 was defined to be 0.1 MPa. The values of B and C were determined by least-squares fitting and are listed in Table 8 for pure substances and in Table 9 for the mixtures. It was found that the Tait equation can be used to represent the experimental results with average deviations of 0.01 %. However, B and C of the mixtures could not be expressed with simple mixing rules.

Some researchers have tried to correlate the excess molar volume with equations of state in conjunction with mixing rules [25–32]. These studies, however, focused on the excess molar volume at normal pressures and only a few discussed about the behavior under high pressure [32]. To elucidate reliable mixing models for the

Table 3 Specific volumes of indole + biphenyl system under pressure at 333.15 K

	Specific volume ($cm^3 \cdot g^{-1}$)				
	Mole fraction of indole				
P (MPa)	0.0000	0.2500	0.5000	0.7500	1.0000
0.1	0.9985	0.9848	0.9698	0.9538	0.9360
10.0		0.9792	0.9648	0.9488	0.9315
20.0		0.9737	0.9601	0.9442	0.9273
30.0			0.9553	0.9399	0.9228
40.0			0.9507	0.9356	0.9192
50.0			0.9464	0.9316	0.9157
60.0			0.9423	0.9278	
70.0			0.9384	0.9241	
80.0			0.9347	0.9205	
90.0				0.9171	
100.0				0.9139	
110.0				0.9108	
120.0				0.9077	
130.0				0.9047	
140.0				0.9020	
150.0				0.8991	
160.0				0.8965	
170.0				0.8939	

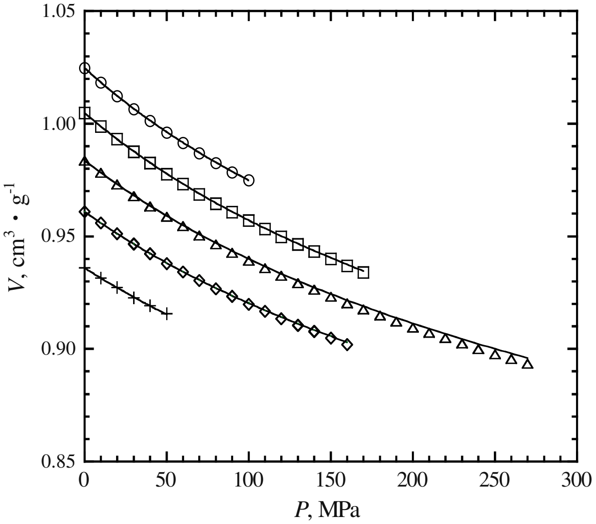

Fig. 1 *PVT* relationships of the indole + 2-methylnaphthalene system at 333.15 K: ○, $x_1 = 0.0000$; □, $x_1 = 0.2500$; Δ, $x_1 = 0.500$; ◇, $x_1 = 0.7500$; +, $x_1 = 1.000$ (x_1 is mole fraction of indole); —, calculated values with the CS–vdW equation of state with the parametersin Tables 10 and 11

Fig. 2 *PVT* relationships of the indole + biphenyl system at 333.15 K: □, $x_1 = 0.2500$; Δ, $x_1 = 0.500$; ◇, $x_1 = 0.7500$; +, $x_1 = 1.000$ (x_1: mole fraction of indole); —, calculated values with the CS–vdW equation of state with the parameters in Tables 10 and 11

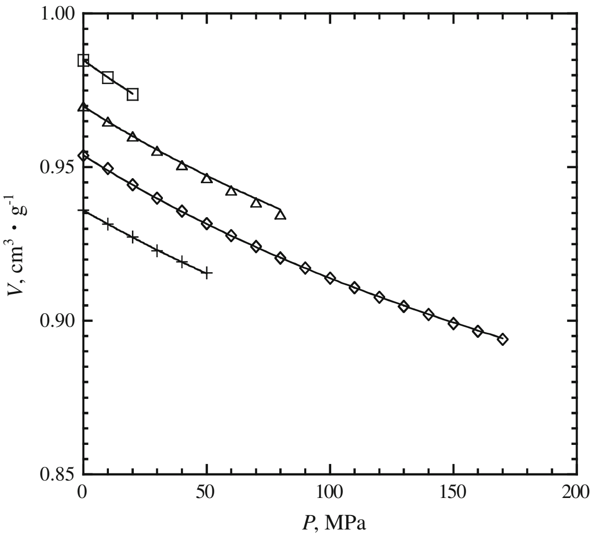

Table 4 Specific volumes of indole, 2-methylnaphthalene, and biphenyl under pressure

	Specific volume ($cm^3 \cdot g^{-1}$)					
	T (K)					
P(MPa)	333.15[a]	343.15	353.15	343.15	353.15	363.16
	Indole			2-methyl -naphthalene	biphenyl	
0.1	0.9360	0.9428	0.9499	1.0326	1.0152	1.0237
10.0	0.9315	0.9381	0.9449	1.0261	1.0084	1.0164
20.0	0.9273	0.9335	0.9402	1.0199	1.0018	1.0096
30.0	0.9228	0.9292	0.9358	1.0136	0.9956	1.0031
40.0	0.9192	0.9249	0.9313	1.0078		0.9970
50.0	0.9157	0.9209	0.9273	1.0026		0.9917
60.0		0.9173	0.9231	0.9977		0.9864
70.0		0.9140	0.9195	0.9932		0.9815
80.0		0.9103	0.9158	0.9885		
90.0			0.9123	0.9843		
100.0			0.9091	0.9802		
110.0			0.9059	0.9764		
120.0				0.9725		
130.0				0.9689		
140.0				0.9655		

[a] Ref. [15]

two mixtures measured in this study, we applied the following CS–vdW equation of state [33]:

$$P = (RT/V)(1 + y + y^2 - y^3)/(1 - y)^3 - a/V^2 \tag{4}$$

Table 5 Specific volumes of indole + 2-methylnaphthalene system at 0.1 MPa

	Specific volume ($cm^3 \cdot g^{-1}$)				
	Mole fraction of indole				
T (K)	0.0000	0.2500	0.5000	0.7500	1.0000
353.15	1.0406	1.0205	0.9983	0.9747	0.9499
343.15	1.0326	1.0126	0.9909	0.9674	0.9428
333.15	1.0247	1.0048	0.9836	0.9609	0.9360
323.15	1.0168	0.9968	0.9765	0.9539	0.9295
313.15	1.0088	0.9893	0.9692	0.9471	
303.15	1.0014	0.9821	0.9621	0.9406	
293.15		0.9744	0.9522		

Table 6 Specific volumes of indole + biphenyl system at 0.1 MPa

	Specific volume ($cm^3 \cdot g^{-1}$)				
	Mole fraction of indole				
T (K)	0.0000	0.2500	0.5000	0.7500	1.0000
363.15	1.0237	1.0086	0.9924	0.9747	
353.15	1.0152	1.0004	0.9848	0.9675	0.9499
343.15	1.0068	0.9924	0.9770	0.9599	0.9428
333.15	0.9985	0.9848	0.9698	0.9538	0.9360
323.15		0.9769	0.9624	0.9462	0.9295
313.15			0.9550	0.9393	
303.15			0.9477	0.9328	

where T is the temperature, P is the pressure, V is the molar volume, and R is the universal gas constant. The reduced density, y, is defined by

$$y = b/4V. \tag{5}$$

In Eqs. 4 and 5, a and b are parameters. The values of the parameters are determined with the method proposed by Ewing and Marsh [26,27] using density and the isothermal compressibility data at 0.1 MPa. The values of the isothermal compressibility were obtained from the Tait equation. Tables 10 and 11 show the values of a and b for pure liquids and binary liquid mixtures, respectively. The CS–vdW equation of state can represent the experimental molar volumes of indole, 2-methylnaphthalene, and biphenyl with average deviations in the range of 0.01 % to 0.04 % and those of the indole + 2-methylnaphthalene and indole + biphenyl systems with average deviations in the range of 0.03 % to 0.12 % and 0.01 % to 0.07 %, respectively. The solid lines in

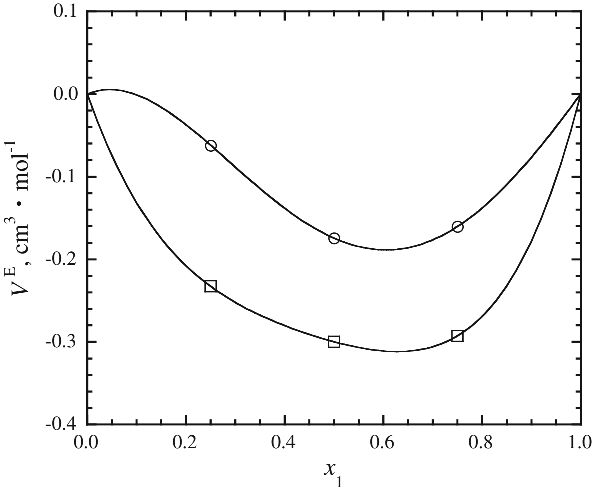

Fig. 3 Excess molar volumes of the indole + 2-methylnaphthalene and indole + biphenyl systems at 353.15 K and at 0.1 MPa (x_1 is mole fraction of indole): ○, indole + 2-methylnaphthalene system; □, indole + biphenyl system; —, calculated values with Eq. 2

Table 7 Parameters of Redlich–Kister type equation for V^E of the indole + 2-methylnaphthalene and indole + biphenyl systems at 0.1 MPa

System	T (K)	a_0 (cm^3 · mol)	a_1 (cm^3 · mol)	a_2 (cm^3 · mol)
Indole + 2-methylnaphthalene	323.15	−0.45647	0.31709	−0.70474
	333.15	−0.54356	0.14372	0.14280
	343.15	−0.59721	−0.41678	0.043080
	353.15	−0.69770	−0.52449	0.41830
Indole + biphenyl	333.15	−0.932344	−0.021648	0.37325
	343.15	−1.18256	−0.49418	−0.82520
	353.15	−1.19934	−0.31982	−0.80808

Figs. 1 and 2 represent the calculated values with the CS–vdW equation of state with the parameters in Tables 10 and 11.

We tried to study the effect of mixing rules on representation of the liquid molar volumes. Since the melting temperature of biphenyl at 0.1 MPa is 343.13 K [12], *PVT* relationships of biphenyl were measured at 353.15 K and 363.15 K. a and b of the CS–vdW equation for biphenyl can be expressed as follows:

$$a = 23.1405 - 0.03147T \tag{6}$$

$$b = 0.480740 - 0.000221T \tag{7}$$

From these equations, the parameter values at 333.15 K were obtained. b of the mixture is expressed as the following mole fraction average:

$$b = x_1 b_1 + x_2 b_2 \tag{8}$$

Table 8 Parameters of the Tait equation for indole, 2-methylnaphthalene, and biphenyl

Substance	T (K)	C	B (MPa)	Ave. dev. (%)[a]	Max. dev. (%)[b]
Indole	333.15	0.08855	179.7	0.01	0.04
	343.15	0.09224	176.2	0.01	0.02
	353.15	0.09335	170.8	0.01	0.02
2-Methylnaphthalene	333.15	0.09050	139.0	0.01	0.04
	343.15	0.08963	131.1	0.01	0.04
Biphenyl	353.15	0.13448	193.6	0.01	0.01
	363.15	0.08785	116.6	0.01	0.03

[a] Ave. dev. = $\Sigma|(V_{\text{exp}} - V_{\text{cal}})/V_{\text{cal}}|/n$, $n =$ number of data points

[b] Max. dev. = Maximum of $|(V_{\text{exp}} - V_{\text{cal}})/V_{\text{cal}}|$

Table 9 Parameters of the Tait equation for indole + 2-methylnaphthalene and indole + biphenyl systems at 333.15 K

System	Mole fraction of Indole	C	B(MPa)	Ave. dev. (%)[a]	Max. dev. (%)[b]
Indole + 2-methylnaphthalene	0.2500	0.08957	142.1	0.01	0.03
	0.5000	0.09037	156.1	0.01	0.02
	0.7500	0.09308	171.5	0.01	0.02
Indole + biphenyl	0.2500	0.12415	209.3	0.0	0.0
	0.5000	0.11703	219.2	0.02	0.04
	0.7500	0.09181	172.9	0.0	0.01

[a] Ave. dev. = $\Sigma|(V_{\text{exp}} - V_{\text{cal}})/V_{\text{cal}}|/n$, $n =$ number of data points

[b] Max. dev. = Maximum of $|(V_{\text{exp}} - V_{\text{cal}})/V_{\text{cal}}|$

Table 10 Parameters of the CS–vdW equation of state for indole, 2-methylnaphthalene, and biphenyl

Substance	T (K)	a ($\text{Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2}$)	$b \times 10^3$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	Ave. dev. (%)[a]	Max. dev. (%)[b]
Indole	333.15	6.89448	0.25309	0.02	0.04
	343.15	6.86770	0.25261	0.01	0.03
	353.15	6.84526	0.25221	0.02	0.04
2-Methylnaphthalene	333.15	9.30138	0.33763	0.01	0.04
	343.15	9.24097	0.33692	0.02	0.04
Biphenyl	356.15	12.0265	0.40269	0.04	0.10
	363.15	11.7179	0.40048	0.04	0.09

[a] Ave. dev. = $\Sigma|(V_{\text{exp}} - V_{\text{cal}})/V_{\text{cal}}|/n$, $n =$ number of data points

[b] Max. dev. = Maximum of $|(V_{\text{exp}} - V_{\text{cal}})/V_{\text{cal}}|$

a was obtained from the following two mixing rules. The first is a conventional one-parameter mixing rule as follows:

$$a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \tag{9}$$

Table 11 Parameters of the CS–vdW equation of state for indole + 2-methylnaphthalene and indole + biphenyl systems at 333.15 K

System	Mole fraction of indole	a $(\mathrm{Pa \cdot m^6 \cdot mol^{-2}})$	$b \times 10^3$ $(\mathrm{m^3 \cdot mol^{-1}})$	Ave. dev. (%)[a]	Max. dev. (%)[b]
Indole + 2-methyl-naphthalene	0.2500	8.54445	0.31505	0.03	0.07
	0.5000	8.05856	0.29480	0.12	0.29
	0.7500	7.45243	0.27374	0.04	0.11
Indole + biphenyl	0.2500	10.8326	0.36528	0.01	0.03
	0.5000	9.77596	0.32938	0.07	0.16
	0.7500	8.08722	0.28925	0.02	0.05

[a] Ave. dev. = $\Sigma|(V_{\mathrm{exp}} - V_{\mathrm{cal}})/V_{\mathrm{cal}}|/n$, n = number of data points

[b] Max. dev. = Maximum of $|(V_{\mathrm{exp}} - V_{\mathrm{cal}})/V_{\mathrm{cal}}|$

Table 12 Interaction parameters for indole + 2-methylnaphthalene and indole + biphenyl systems at 333.15 K

System	Mole fraction of indole	k_{12}	l_{12}	Ave. dev. (%)[a]	Max. dev. (%)[b]
Indole + 2-methyl-naphthalene	0.2500			0.14	0.25
	0.5000	−0.0182	–	0.19	0.38
	0.7500			0.07	0.17
Indole + 2-methyl-naphthalene	0.2500			0.13	0.25
	0.5000	−0.0202	0.0041	0.19	0.38
	0.7500			0.08	0.17
Indole + biphenyl	0.2500			0.07	0.12
	0.5000	−0.0603	–	0.13	0.24
	0.7500			0.18	0.34
Indole + biphenyl	0.2500			0.04	0.09
	0.5000	−0.0669	0.0088	0.11	0.22
	0.7500			0.18	0.34

[a] Ave. dev. = $\Sigma|(V_{\mathrm{exp}} - V_{\mathrm{cal}})/V_{\mathrm{cal}}|/n$, n = number of data points

[b] Max. dev. = Maximum of $|(V_{\mathrm{exp}} - V_{\mathrm{cal}})/V_{\mathrm{cal}}|$

$$a_{12} = (1 - k_{12})\sqrt{a_{11}a_{22}} \tag{10}$$

where k_{12} is a binary interaction parameter. The second model is the two-parameter mixing rule proposed by Adachi and Sugie [29]. In this model, a_{12} can be expressed as follows:

$$a_{12} = (1 - (k_{12} + l_{12}x_1))\sqrt{a_{11}a_{22}} \tag{11}$$

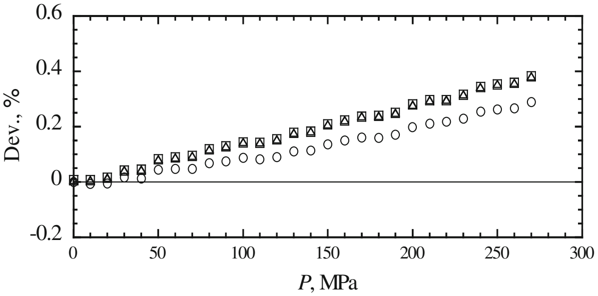

Fig. 4 Deviations of the calculated molar volumes with the CS–vdW equation of state from the experimental values of the indole (0.5000) + 2-methylnaphthalene (0.5000) system at 333.15 K: ◯, calculated results with the a, b parameters in Tables 10 and 11; □, calculated results with Eqs. 8–10; Δ, calculated results with Eqs. 8, 9, and 11

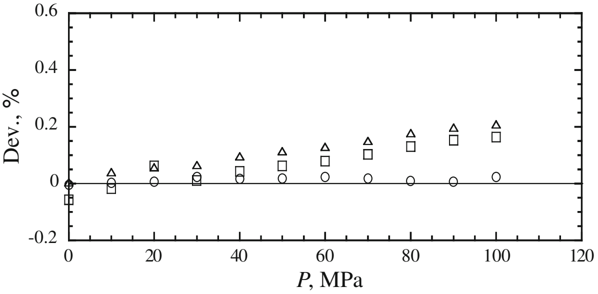

Fig. 5 Deviations of the calculated molar volumes with the CS–vdW equation of state from the experimental values of the indole (0.7500) + biphenyl (0.2500) system at 333.15 K: ◯, calculated results with the a, b parameters in Tables 10 and 11; □, calculated results with Eqs. 8–10; Δ, calculated results with Eqs. 8, 9, and 11

where k_{12} and l_{12} are binary interaction parameters. Since this model has two parameters, the non-ideal behavior of excess thermodynamic properties can be described with more flexibility than for the one-parameter model. The values of k_{12}, or k_{12} and l_{12} were determined by least-squares fitting. The optimum values of the parameters and deviations are listed in Table 12. Figures 4 and 5 show deviation plots for the indole (0.5000) + 2-methylnaphthalene (0.5000) and indole (0.7500) + biphenyl (0.2500) systems, respectively. As can be seen, the CS–vdW equation of state with these two simple mixing rules can reproduce the molar volume of liquid mixtures with reasonable accuracy, while the calculated results for the case when both parameters, a and b, were fitted to the experimental volume and isothermal compressibility at 0.1 MPa is better than those with parameters obtained from the mixing rules. From the comparison between Eqs. 10 and 11, the two-parameter model did not show much improvement. This may be due to the fact that the two mixtures investigated in this study behave as nearly ideal systems and also due to the inability of the CS–vdW equation to represent the *PVT* relationships of pure substances with high accuracy.

The excess molar volume can be calculated with the CS–vdW equation of state. Figure 6 shows the calculated results for the indole (0.5000) + 2-methylnaphthalene (0.5000) and indole (0.7500) + biphenyl (0.2500) systems. The mixing rule used was

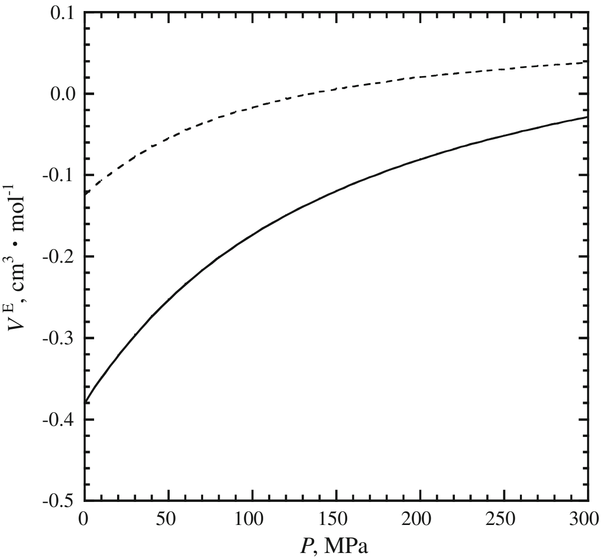

Fig. 6 Excess molar volumes of the indole (0.5000) + 2-methylnaphthalene (0.5000) and indole (0.7500) + biphenyl (0.2500) systems calculated with the CS–vdW equation of state: —, indole (0.7500) + biphenyl (0.2500) system; - - -, indole (0.5000) + 2-methylnaphthalene (0.5000) system

Eqs. 8–10. The molar volumes of biphenyl and indole above the melting pressures should be considered as those of super-compressed liquids. As can be seen from these figures, the excess molar volume increases with increasing pressure and seems to approach a limiting value.

5 Conclusion

PVT relationships have been measured for binary liquid mixtures of indole with 2-methylnaphthalene and with biphenyl in the temperature range from 293.15 K to 363.15 K at 0.1 MPa, and at 333.15 K and at pressures up to 270 MPa or up to the freezing pressures. The excess molar volumes V^E at 0.1 MPa were obtained from the present experimental data. It was found that the excess molar volumes were negative for these mixtures, which were correlated with a Redlich–Kister type equation. The *PVT* data were represented with the Tait equation and the CS–vdW equation of state. As for the CS–vdW equation, the effect of mixing rules was investigated. It was found the conventional simple mixing rule with one or two interaction parameters can give reasonably good agreement with the experimental results.

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