

# MONTE CARLO CALCULATION OF SOLUBILITIES OF HIGH-BOILING COMPONENT IN SUPERCRITICAL CARBON DIOXIDE AND SOLUBILITY ENHANCEMENTS BY ENTRAINER

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The restricted umbrella sampling method proposed by Shing and Gubbins was applied to calculate the solubilities of hexamethylbenzene and those of phenanthrene in supercritical carbon dioxide. It was also used to calculate solubility enhancements of phenanthrene by the addition of octane in supercritical carbon dioxide. The Lennard-Jones (12-6) potential was used as the intermolecular potential and the Lorentz-Berthelot mixing rule was adopted for unlike molecular pairs. The solubilities of phenanthrene and those of hexamethylbenzene in supercritical carbon dioxide were calculated quantitatively by introducing only a binary interaction parameter between unlike molecules. Furthermore, the entrainer effects calculated by the Monte Carlo simulation show good agreement with the experimental data.

## Introduction

Separation methods for high-boiling components have generated considerable interest in recent years. Supercritical fluid extraction shows promise of being a new separation method and has the following advantages. Solvent recovery can be easily achieved either by decompression or by temperature change. Because of the high volatility of supercritical fluid there is little solvent contamination of the product extracted. Solubility data of high-boiling components in supercritical fluids are very important as fundamental data, although the apparatus for high-pressure measurements may be expensive. However, computer simulation may be feasible for obtaining thermodynamic data for mixtures. The supercritical fluid extraction method is used to separate certain components from a condensed phase which may be solid or liquid. In this work the authors studied the case in which the condensed phase is a solid consisting of pure high-boiling component. Since the supercritical fluid can be assumed to be insoluble in the solid, the fugacity or chemical potential of solid component in the solid phase can be obtained from the properties of the pure component. Computer simulation is only necessary to calculate the fugacity or chemical potential of solid component in the supercritical fluid phase. Furthermore, the simulation can be easily achieved because the solubility of solid component in supercritical fluid is usually

very low and the composition of solid component can be assumed to be infinite dilution.

Recently, Shing and Chung<sup>13)</sup> applied Widom's test-particle method and the Kirkwood method to calculate the solubilities of naphthalene in supercritical carbon dioxide. Nouacer and Shing<sup>9)</sup> calculated the solubilities of naphthalene in supercritical carbon dioxide + water mixture by the Grand Canonical Ensemble Monte Carlo method. However, they did not optimize the potential parameters, and the calculated results were not in good agreement with the experimental data. In a previous work<sup>5)</sup>, the authors applied the test-particle method proposed by Widom<sup>16)</sup> to calculate the solubilities of naphthalene in supercritical carbon dioxide at 308.15 and 328.15 K and showed that the calculation results were in good agreement with the experimental data when a binary interaction parameter was introduced between carbon dioxide and naphthalene. In this work, the solubilities of hexamethylbenzene in supercritical carbon dioxide were calculated by the test-particle method and the restricted umbrella sampling (RUS) method proposed by Shing and Gubbins<sup>14)</sup> so as to compare the results of these methods. Furthermore, the solubilities of phenanthrene in supercritical carbon dioxide and the entrainer effect of octane were calculated by the RUS method.

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**Table 1.** Critical constants and potential parameters

Component	$T_C$ (K)	$P_C$ (MPa)	$\sigma$ (Å)	$\varepsilon/k$ (K)
CO <sub>2</sub>	304.2 <sup>(1)</sup>	7.37 <sup>(1)</sup>	3.91	225.3
Hexamethylbenzene	751.1 <sup>(2)</sup>	2.38 <sup>(2)</sup>	7.70	556.4
Phenanthrene	878.0 <sup>(1)</sup>	2.90 <sup>(2)</sup>	7.60	650.4
Octane	568.8 <sup>(1)</sup>	2.48 <sup>(1)</sup>	6.93	421.3

## 1. Method

### 1.1 Potential parameter

The Lennard-Jones (12-6) potential was used for all particles:

$$\phi_{ij} = 4 \varepsilon_{ij} \left\{ \left( \sigma_{ij} / r_{ij} \right)^{12} - \left( \sigma_{ij} / r_{ij} \right)^6 \right\} \quad (1)$$

where  $\phi$  is the intermolecular potential,  $\varepsilon$  the energy parameter,  $\sigma$  the size parameter, and  $r_{ij}$  the intermolecular distance between molecules  $i$  and  $j$ .

When the following reduced variables are used, the corresponding-state principle assures that all Lennard-Jones fluids for pure components obey the same reduced equation of state:

$$\rho^* = N \sigma^3 / V, \quad T^* = kT / \varepsilon, \quad P^* = \sigma^3 P / \varepsilon \quad (2)$$

where  $\rho$  is the density,  $N$  the number of particles,  $V$  the volume,  $k$  the Boltzmann constant,  $T$  the temperature and  $P$  the pressure. Superscript \* means the reduced property. Nicolas *et al.*<sup>(8)</sup> proposed reduced critical constant values of  $\rho_C^*$ ,  $T_C^*$ , and  $P_C^*$  at the critical point as 0.35, 1.35, and 0.1418 respectively. In this work the pure-component parameters were calculated using  $T_C$  and  $P_C$  because the values of  $T_C$  and  $P_C$  are more reliable than that of  $V_C$ . The values of critical constants and potential parameters adopted in this study are listed in **Table 1**.

According to the Lorentz-Berthelot rule, the potential parameters between components  $i$  and  $j$  are given as follows.

$$\sigma_{ij} = 0.5 (\sigma_{ii} + \sigma_{jj}) \quad (3)$$

and

$$\varepsilon_{ij} = (1 - k_{ij}) (\varepsilon_{ii} \varepsilon_{jj})^{1/2} \quad (4)$$

where  $k_{ij}$  is the binary interaction parameter between unlike molecules  $i$  and  $j$ .

### 1.2 Residual chemical potential

Shing and Gubbins<sup>(14)</sup> proposed the restricted umbrella sampling (RUS) method to calculate chemical potential in dense fluid where Widom's test-particle method fails. In this work, the authors adopted the RUS method to calculate the chemical potential of high-boiling component in supercritical fluid. The RUS method is explained briefly. In the simulation, the authors used the canonical ( $NVT$ ) ensemble. The standard Metropolis "importance sampling" method was used to obtain new configurations. After a large number of configurations were generated to reach equilibrium condition, a test particle was inserted. For every 50 con-

figurations of the real particles, a test particle was placed at random locations until the potential energy  $\psi$  experienced by the test particle was lower than  $\psi_{max}$ . Then it was set in random movement within its neighborhood. The movement of the test particle was accepted when  $\psi$  at a new position was lower than  $\psi_{max}$ . When  $\psi$  at the new position was higher than  $\psi_{max}$ , the movement was rejected and the test particle was returned to the previous position. For each fixed configuration of 108 real particles, the test particle moved 55 times. Five movements immediately after introducing the test particle were neglected in order to allow the system to equilibrate.

The residual chemical potential of test particle component  $i$ ,  $\mu_i^r$ , was calculated by the following equation.

$$\mu_i^r = -kT \ln \{ \langle \exp(-\psi/kT) \rangle_{108} / W \} \quad (5)$$

where  $\langle \rangle_{108}$  is a canonical ensemble average of the system of 108 real particles and  $W$  is calculated by the following equation.

$$W = f_w(\psi) / f(\psi) \quad (6)$$

where  $f_w(\psi)$  and  $f(\psi)$  are the distribution function of  $\exp(-\psi/kT)$  for weight and uniform sampling respectively.

### 1.3 Calculation of solubility

The residual chemical potential of solute 2 (high-boiling component),  $\mu_2^r$ , can be related to Henry's constant  $H_2$  at infinite dilution:

$$H_2 = \rho kT \exp(\mu_2^r / kT) \quad (7)$$

where  $\rho$  is the number density in supercritical phase. The solubility of high-boiling component  $y_2$  is usually very low. Therefore,  $y_2$  can be calculated by the following equation.

$$y_2 = f_2^G / H_2 \quad (8)$$

where  $f_2^G$  is the fugacity of component 2 in the gas phase. Since the fugacities of component 2 in the gas phase and the solid phase for pure high-boiling component are equal, the next equation is obtained.

$$f_2^G = f_2^S = P_2^{sat} \exp \left\{ \frac{v_2^S (P - P_2^{sat})}{RT} \right\} \quad (9)$$

where  $P^{sat}$  is the saturation pressure,  $v$  the molar volume,  $R$  the gas constant, and superscript  $S$  means the solid state.

From Eqs. (7)-(9) the solubility of high-boiling component 2 is given as follows:

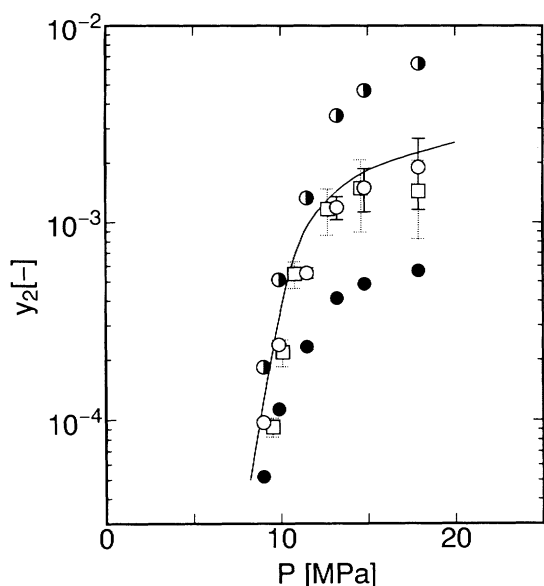
$$y_2 = \frac{P_2^{sat}}{H_2} \exp \left\{ \frac{v_2^S (P - P_2^{sat})}{RT} \right\} \quad (10)$$

### 1.4 Pressure

The pressure of the system can be calculated from

$$\frac{P_V}{RT} = 1 - \frac{2\pi N}{3V_0 kT} \sum \sum y_i y_j \frac{d\phi_{ij}}{dr} g_{ij} r^3 dr \quad (11)$$

where  $V_0$  is the volume of the cell,  $N$  the number of real



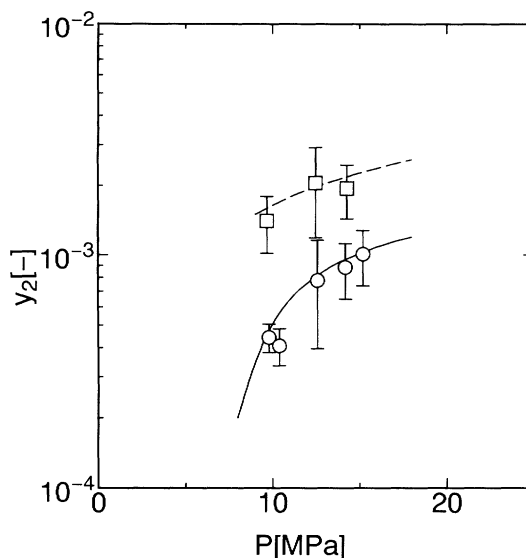
**Fig. 1** Solubility of hexamethylbenzene in supercritical  $\text{CO}_2$  at 323.15 K: —, experimental data<sup>6)</sup>; ●, ○, ●, Monte Carlo calculation by RUS method with  $k_{12} = 0.10, 0.15, 0.20$ , respectively; □, Monte Carlo calculation by Widom's method with  $k_{12} = 0.15$ ; Vertical lines represent 95 % confidence limits

particles in the cell,  $y$  the mole fraction,  $r$  the distance, and  $g_{ij}$  the radial distribution function. Half of the side length of the cell was used for cut-off distance  $r_{\text{cut}}$ . Contributions to the energy and pressure for  $r > r_{\text{cut}}$  were corrected by assuming that  $g_{ij} = 1$  in the region.

## 2. Results and Discussion

### 2.1 Supercritical $\text{CO}_2$ (1) + hexamethylbenzene (2) system

The RUS method was applied to calculate the solubilities of hexamethylbenzene in supercritical carbon dioxide at 323.15 K. The value of  $v_2^S$  is  $152.7 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $P_2^{\text{sat}}$  at 323.15 K is 2.3853 Pa from the literature data of Weast and Astle<sup>15)</sup> and Ambrose *et al.*<sup>1)</sup>, respectively. The length of the calculation was  $2 \times 10^6$  configurations for the lower-density region of carbon dioxide, i.e., the pressure was less than 12 MPa. For the higher-density region, it was  $3 \times 10^6$  configurations. The initial  $2 \times 10^5$  configurations were neglected to attain equilibrium. The 95 % confidence limits for the residual chemical potential are calculated by using the overall averaged for  $\exp(-\psi/kT)$  and sub-averaged for every  $10^4$  insertions. **Figure 1** shows the calculated results with various values of  $k_{12}$ . As shown in this figure, the solubilities calculated with  $k_{12} = 0.15$  are in good agreement with the experimental data. The calculated results by Widom's test-particle method are also shown in Fig. 1. Details of Widom's method and calculation procedure were given in previous work<sup>5)</sup> in which the solubilities of naphthalene in supercritical carbon dioxide were calculated. The length of the calculation was longer, because the diameter of hexamethylbenzene is larger than that of naphthalene and it



**Fig. 2** Solubility of phenanthrene in supercritical  $\text{CO}_2$  + octane at 308.15 K: —, ---, experimental data<sup>3,4)</sup>, mole fractions of octane in gas phase are 0 and 0.035, respectively; ○, □, Monte Carlo calculation by RUS method, mole fractions of octane in gas phase are 0 and 4/108, respectively; Vertical lines represent 80 and 50 % confidence limits, respectively

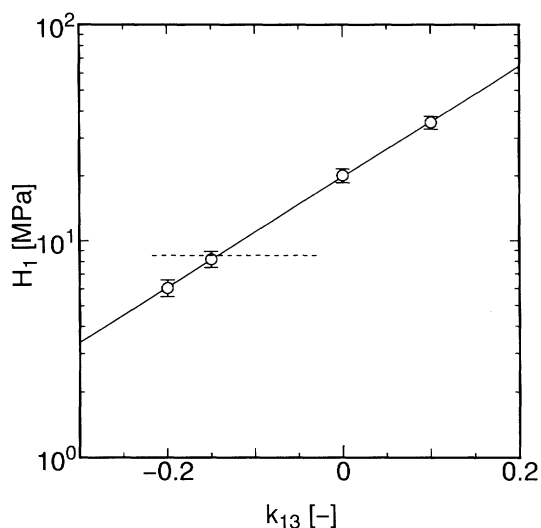
becomes difficult to insert hexamethylbenzene in supercritical  $\text{CO}_2$ . The lengths of the calculations were  $3 \times 10^6$  and  $1 \times 10^6$  configurations when the pressure ranges were higher than 12 MPa and less than 12 MPa, respectively. Widom's method gives results similar to those by the RUS method except for the highest density (highest pressure) when the same value of binary interaction parameter  $k_{12}$  is used. However, the 95 % confidence limits by Widom's method are higher than those by the RUS method. At the highest density the reliability of Widom's method was less satisfactory. Therefore, the authors adopted the RUS method for the following systems.

### 2.2 Supercritical $\text{CO}_2$ (1) + phenanthrene (2) system

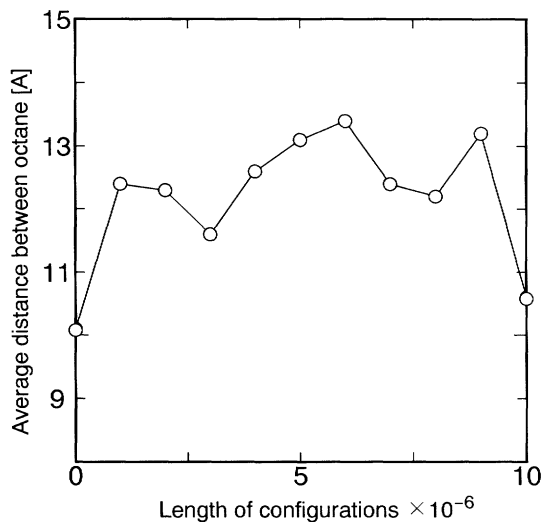
The RUS method was applied to calculate the solubilities of phenanthrene in supercritical carbon dioxide at 308.15 K. The value of  $v_2^S$  is  $151.2 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $P_2^{\text{sat}}$  at 308.15 K is  $6.585 \times 10^{-2}$  Pa from the literature data of Perry *et al.*<sup>10)</sup> and Kudchadker *et al.*<sup>7)</sup>, respectively. The value of  $k_{12}$  was adjusted to give good representation of the experimental data of the solubilities of phenanthrene in supercritical carbon dioxide. As shown in **Fig. 2**, the calculated solubilities are in good agreement with the experimental data when 0.14 is used for  $k_{12}$ .

### 2.3 Supercritical $\text{CO}_2$ (1) + phenanthrene (2) + octane (3) system

The solubility of phenanthrene in supercritical carbon dioxide increases by the addition of octane in supercritical phase. This is well known as the entrainer effect. Before calculation of the entrainer effect, the binary interaction parameter between  $\text{CO}_2$  and octane,  $k_{13}$ , was estimated. Henry's constant for  $\text{CO}_2$  gas in liquid octane at low pressure and 308.15 K was calcu-



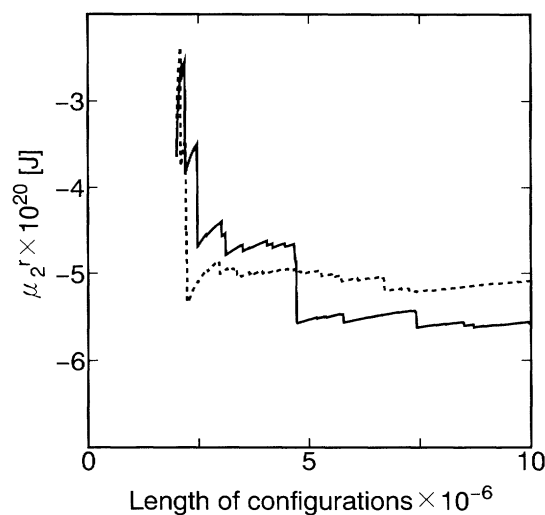
**Fig. 3** Relationship between Henry's constant of  $\text{CO}_2$  in liquid octane and binary interaction parameter  $k_{13}$  at 308.15 K and low pressure: ---, experimental datum<sup>17)</sup>; ○, Monte Carlo calculation; Vertical lines represent 95 % confidence limits; —, smoothed line



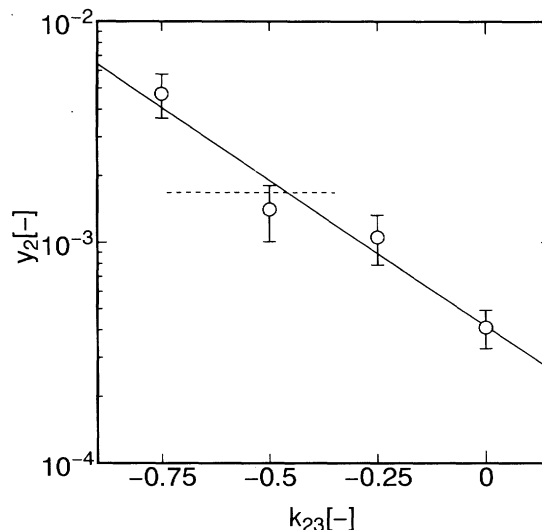
**Fig. 4** Averaged distance of octane particles at 308.15 K: Molar volume is  $70 \text{ ml} \cdot \text{mol}^{-1}$  and pressure is 9.8 MPa, Four particles of octane and 104 particles of  $\text{CO}_2$  are in cell; ○, Monte Carlo calculation

lated by the RUS method. As shown in **Fig. 3** the value of  $k_{13}$  was determined as  $-0.14$  to give good representation of interpolated data<sup>17)</sup> of Henry's constant at 308.15 K.

Dobbs *et al.*<sup>4)</sup> measured the solubility of phenanthrene in supercritical carbon dioxide + octane phase. The mole fraction of octane in the gas phase was 0.035. To calculate the entrainer effect, 104 particles of carbon dioxide and four particles of octane were set in the cell. In the simulation, the mole fraction of octane was 0.037, slightly higher than the experimental condition. The average distance between the four particles of octane is shown in **Fig. 4**. As shown in this figure, the particles of octane may not reach aggregation state. Long length of configurations is usually needed for the binary system of

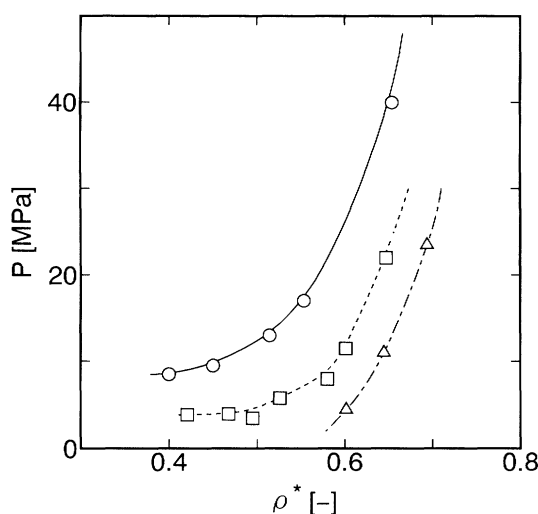


**Fig. 5** Averaged values of residual chemical potential of phenanthrene in supercritical  $\text{CO}_2$  + octane at 308.15 K as function of length of configurations: Mole fraction of octane in gas phase is 4/108; ---, Molar volume of gas phase is  $70 \text{ ml} \cdot \text{mol}^{-1}$  and pressure is 9.8 MPa; —, Molar volume of gas phase is  $67 \text{ ml} \cdot \text{mol}^{-1}$  and pressure is 14.3 MPa



**Fig. 6** Relationship between solubility of phenanthrene in supercritical  $\text{CO}_2$  + octane and binary parameter  $k_{23}$  at 308.15 K and 9.8 MPa: ---, experimental datum<sup>4)</sup>; ○, Monte Carlo calculation; Vertical lines represent 50 % confidence limits; —, smoothed line

real particles to reach equilibrium condition compared with the single system of real particles, because it may take a long time to become random mixture. First of all, the calculation of solubilities of phenanthrene at 9.8 MPa was carried out with  $k_{23} = 0.0$ . The result of the chemical potential calculated by  $1 \times 10^7$  configurations was almost the same as that by  $4 \times 10^6$  configurations as shown in **Fig. 5**. So the authors additionally calculated the chemical potentials at three values of  $k_{23}$  by  $4 \times 10^6$  configurations to show the dependence of values of  $k_{23}$  for the solubilities. The calculated results are shown in **Fig. 6**. The value of  $k_{23}$  was determined to be  $-0.45$ . The



**Fig. 7** PVT relationship of CO<sub>2</sub> + octane system at 308.15 K: ○, □, △, Monte Carlo calculation, mole fractions of octane are 0, 4/108, and 6/108, respectively; —, ---, — — —, smoothed lines

solubilities of phenanthrene in supercritical carbon dioxide with octane were calculated at higher pressure at that value of  $k_{23}$ . The calculated results of solubilities are shown in Fig. 2. The experimental results are in good agreement with the experimental data when the mole fraction of octane is 0.035 in the gas phase. Long length of configurations is necessary at high pressure, i.e., high density. The change in chemical potential with the length of configurations are shown in Fig. 5 when the pressure was 14.3 MPa as an example.

As obtained above, the binary interaction parameters are  $k_{12} = 0.14$ ,  $k_{13} = -0.14$  and  $k_{23} = -0.45$ . Essentially,  $k_{ij}$  may be expected to be slightly positive. However,  $k_{13}$  determined by Henry's constant is negative. Further,  $k_{23}$  is highly negative. This may be due to the fact that the value of  $k_{23}$  was indirectly determined by using the ternary system data. At present it seems difficult to estimate the value of  $k_{ij}$  based on some rule. It should be evaluated by fitting the model to accurate experimental data.

The authors tried to calculate the solubilities of phenanthrene in which the mole fraction of octane in gas phase is 0.0525. However, the calculated results showed serious fluctuation. **Figure 7** shows the relationship between the reduced density and pressure for the CO<sub>2</sub> + octane system. The volume of octane particle is much larger than that of carbon dioxide particle. Therefore, the free volume is reduced according to the increase in concentration of octane. This means that it is difficult to insert phenanthrene particle in the high-concentration condition of octane, and serious fluctuations occur in the canonical ensemble average in Eq. (5). The RUS method cannot give reliable results in that case.

## Conclusions

The restricted umbrella sampling (RUS) method

proposed by Shing and Gubbins was applied to calculate the solubilities of hexamethylbenzene in supercritical carbon dioxide. It was shown that the RUS method gave reliable results. The method was also used to calculate the solubilities of phenanthrene and solubility enhancements by addition of octane in supercritical carbon dioxide. The Lennard-Jones (12-6) potential was used as intermolecular potential and the Lorentz-Berthelot mixing rule was adopted for unlike molecular pairs. By introducing the binary parameter between unlike molecules, the calculated results showed good agreement with the experimental data.

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## Nomenclature

$f$	= fugacity	[Pa]
$f(\psi)$	= uniform distribution function	[-]
$f_w(\psi)$	= weighted distribution function	[-]
$g$	= radial distribution function	[-]
$H$	= Henry's constant	[Pa]
$k$	= Boltzmann constant	[J·K <sup>-1</sup> ]
$k_{ij}$	= binary interaction parameter	[-]
$N$	= number of particles	[-]
$P$	= pressure	[Pa]
$r$	= distance between particles	[m]
$R$	= gas constant	[J·mol <sup>-1</sup> ·K <sup>-1</sup> ]
$T$	= absolute temperature	[K]
$V_o$	= volume of cell	[m <sup>3</sup> ]
$v$	= molar volume	[m <sup>3</sup> ·mol <sup>-1</sup> ]
$W$	= weight	[-]
$y$	= mole fraction in supercritical fluid phase	[-]
$\epsilon$	= energy parameter	[J]
$\mu'$	= residual chemical potential	[J]
$\rho$	= density	[m <sup>-3</sup> ]
$\sigma$	= size parameter	[m]
$\phi$	= intermolecular potential	[J]
$\psi$	= potential energy experienced by test particle	[J]
$\psi_{max}$	= maximum value of potential energy experienced by test particle	[J]

## <Superscripts>

$G$	= gas phase
$S$	= solid phase
$sat$	= saturation
$*$	= reduced value

## <Subscripts>

$C$	= critical property
$i, j$	= components $i$ and $j$
1	= supercritical carbon dioxide
2	= high-boiling component (hexamethylbenzene or phenanthrene)
3	= entrainer (octane)

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