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Solubility and Partial Molar Volumes of Heavy Aromatic Hydrocarbons in Supercritical CO_2

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Isothermal solubility data of naphthalene, dibenzothiophene, and mixture of naphthalene + dibenzothiophene in supercritical CO_2 were measured over a pressure range of 75–275 bar. The solubility data have been used to calculate the partial molar volumes. The calculated partial molar volumes of naphthalene in supercritical CO_2 have been compared with the experimental values available in the literature. The calculated values are in good agreement with the experimental values available in the literature.

Introduction

The current interest in the application of supercritical extraction to various processes has attracted the attention of several investigators to work with model compounds and with actual materials like coal. The study of model compounds is an essential part in developing predictive methods. Among the model compounds studied, attention has been focused on two-ring compounds like naphthalene and methyl-substituted naphthalenes (*1*, *2*) and three-ring compounds like phenanthrene (*3*). Kurnik et al. (*2*) summarize the literature on model compounds until 1981. Recently, King and Bott (*4*), Mackay and Paulaitis (*5*), and others have also worked with model compounds, and the results are published in a monograph (*6*). However, model sulfur compounds and mixtures containing sulfur compounds have not been studied so far. This paper presents experimental data on the solubility of naphthalene, dibenzothiophene, and their mixture in supercritical carbon dioxide.

Equations of state, particularly the Soave modification of Redlich–Kwong equation and the Peng–Robinson equation, have been used to predict solubility data. The interaction coefficient in the mixing rule for combining the equation of state constants has to be evaluated by using solubility data. A similar procedure is used for predicting partial molar volumes (*7*). However, it would be extremely valuable if partial molar volumes could be evaluated from experimental solubility data. This paper presents a method for calculating partial molar volumes using experimental solubility data.

Experimental Section

A schematic diagram of the experimental setup consisting of the pressurizing system, temperature-controlled equilibrium cell system, and the pressure releasing system is shown in Figure 1. The equilibrium cell was a standard (Cnix-9906) Autoclave reactor of 15.25 cm length and 2.12 cm internal diameter immersed in a constant temperature bath provided with Model-705 Gulton temperature controller. The high-pressure solvent at ambient temperature was compressed by using a Haskel air-driven compressor. The solute was packed in the cell with quartz wool to plug each end. Sintered stainless steel filters (5 μm) were used to prevent any carryover of the solute. At the desired temperature, the reactor was pressurized with the solvent and the system allowed to equilibrate for 2 h. At the end of the 2-h period, CO_2 was passed at low rates. To ensure that the flow rate did not affect solubility measurements, experiments were conducted at different flow rates between 0.8 and 2.1 cm^3/s. In the case of naphthalene at 75 bar and dibenzothiophene at 172 bar, no detectable variation in solubility at different flow rates could be measured. Therefore, for all solubility measurements, flow rates below 0.7 cm^3/s were used. Gas volumes were measured by using a wet-test meter at ambient temperatures and corrected for the partial pressure of water. The materials used were ACS reagent grade chemicals. Pressures were measured in pounds per square inch and reported in bar. Pressures were measured to an accuracy better than ±0.5 bar and temperatures to ±0.1 K. The purity of carbon dioxide was better than 99.9 mol %. Weighings were done with precision analytical balance accurate to ±0.0001 g. The loss of weight in the experiments ranged from 0.08 to 0.3 g. In the case of the naphthalene + dibenzothiophene mixture, the gas mixture was bubbled through toluene contained in the separator and analyzed by HPLC.

During depressurization of the cell when the pressure is reduced from the high pressure to atmospheric pressure, there can be some recondensation. This introduces an error if the mass in the reactor is used directly for calculation. To compensate for this error blank runs were carried out. These runs were carried out by packing the reactor with the solute and allowing it to stand under the solvent pressure for 1 h and then depressurizing it. The loss of weight thus found was used to correct the error due to the nonequilibrium conditions that prevailed due to depressurization.

Results and Discussion

The experimental solubility values for naphthalene, dibenzothiophene, and naphthalene + dibenzothiophene are recorded in Table I. There was no evidence of solid solution formation in the case of the mixture. The data on naphthalene from the present measurements and from different literature sources plotted in Figure 2 show good agreement among the different sets of data. In absence of sound theoretical basis, it is generally believed that the increased dissolution of solutes in supercritical solvents is primarily due to the highly nonideal behavior of the supercritical solvent phase and the nonideal behavior of the solute–solvent interactions. Under these circumstances, the nonideal behavior should increase for binary mixture of solutes compared to pure solutes, thus increasing the solubility of a mixture. This behavior is documented in the literature (*8*). Table I does, indeed, show increased solubility

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Table I. Experimental Solubility Data in Supercritical CO_2

	mole fraction of solute, 10^4X_2						
	naphthalene		dibenzothiophene			mixture	
P, bar	309.15 K	328.15 K	309.15 K	328.15 K	338.15 K	309.15 K	ratio[a]
76.85	8.04[b]	13.89	0.28	0.19	0.22	0.36	0
104.44	100.0	34.70	4.86	1.51	0.84	186.0	0.0531
138.91	132.3	233.4	9.74	9.17	6.25	239.0	0.1112
173.38	148.9	351.6	10.53	13.90	14.10		
207.86	175.4	447.7	12.50	21.20	22.0	373.0	0.1103
242.33	187.6	506.7	15.30	22.30	24.4		
276.80	196.1	550.4	22.95	23.40	32.2	465.0	0.1194

[a] Ratio = moles of dibenzothiophene to moles of naphthalene. [b] At 75.4 bar.

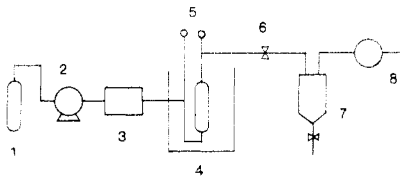

Figure 1. Schematic diagram of the apparatus: (1) CO_2 tank; (2) Haskel compressor; (3) ballast chamber; (4) temperature-controlled reactor system; (5) pressure gauges; (6) metering valve; (7) separator; (8) wet test meter.

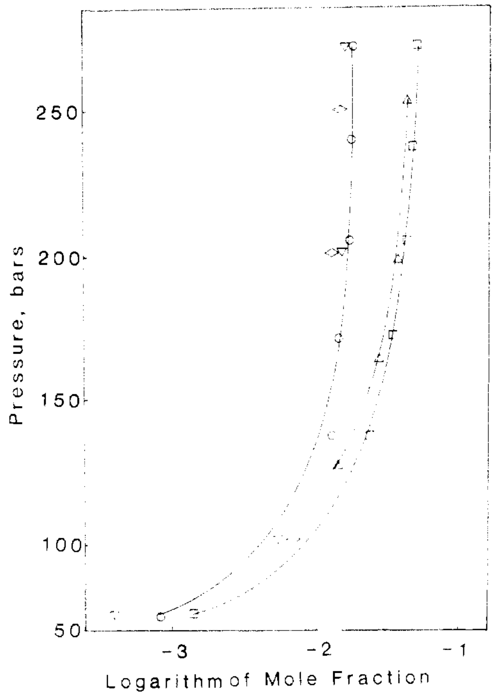

Figure 2. Solubility of naphthalene in CO_2. Comparison of results from different investigations: ▽, Hong et al. (*10*) at 311 K; ◇, King et al. (*4*) 305.3 K; ○, present work at 309.15 K; □, present work at 328.15 K; △, Tsekhanskaya et al. (*9*) at 328 K.

for the mixture compared to the pure solutes. The increase in the ratio of the solubility of the mixture to the solubility of naphthalene with increase in pressure is another indication of the highly nonideal behavior of the solvent–solute interaction. This ratio increases from 1.86 at 104 bar to nearly 2.5 at 276 bar. However, the ratio of the moles of dibenzothiophene to moles of naphthalene remains substantially constant. The strong nonideal behavior is further relfected by the rather large negative values of partial molal volumes around the supercritical region (Figure 3).

The equilibrium relation

$$f_2^s = f_2^f$$

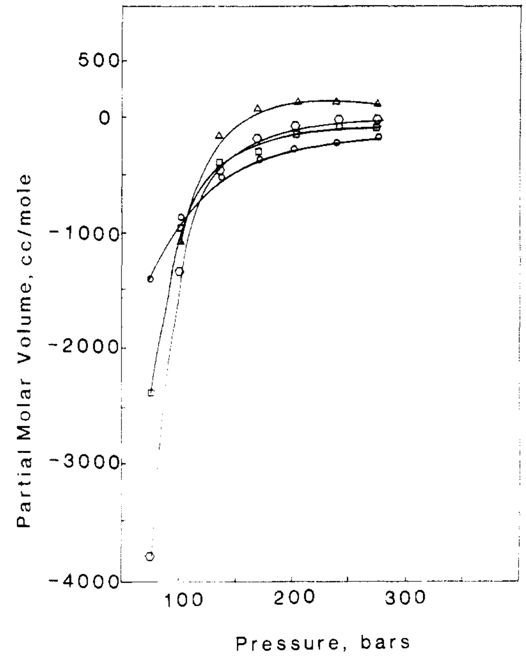

Figure 3. Variation of partial molar volume with pressure at constant temperature: △, dibenzothiophene at 309.15 K; ○, dibenzothiophene at 328.15 K; ○, dibenzothiophene at 338.15 K; □, naphthalene at 328.15 K.

for the solute in the solid and the fluid phases can be written as

$$f_2^s = f_0^s \exp[V_2^s(P - P_0)/RT] \qquad (1)$$

$$f_2^f = f_0^f X_2 \gamma_2 \exp\left[\int_{P_0}^{P} (\bar{V}_2/RT)\, dP\right] \qquad (2)$$

These relations give (*5*)

$$X_2 = \frac{f_0^s \exp[V_2^s(P - P_0)/RT]}{f_0^f \gamma_2 \exp\left[\int_{P_0}^{P} (\bar{V}_2/RT)\, dP\right]} \qquad (3)$$

The reference pressure P_0 is arbitrary and has been taken as P_c, the critical pressure of the solvent; then the value of X_2 (close to $P = P_c$) gives the value of $(f_0^s/f_0^f\gamma_2)$, as both the exponential terms approach unity. Since the values of X_2 at any particular temperature over the experimental range of pressures is small, γ_2 is taken to be independent of composition. Under these conditions we can write

$$\exp \int_{P_c}^{P} (\bar{V}_2/RT)\, dP = \frac{k}{X_2} \exp[V_2^s(P - P_c)/RT] \qquad (4)$$

where $k = [f_0^s/f_0^f\gamma_2]$. It is further assumed that the effect of pressure on V_2^s is negligible. With this, the experimental iso-

Table II. Values of the Constants in Eq 6

system	T, K	$B_1 \times 10^{-8}$	$C_1 \times 10^{-9}$
CO_2 + naphthalene	309.15	0.2014	−3.0
	328.15	−0.00128	−1.0044
CO_2 + dibenzothiophene	309.15	0.2438	−3.624
	328.15	0.0738	−2.153
	338.15	−0.1164	0.288
CO_2 + naphthalene + dibenzothiophene	309.15	0.1670	−2.365

thermal X_2 values at various pressures allow one to evaluate $\exp[\int_{P_c}^{P}(\bar{V}_2/RT)\,dP]$ values. Then it is possible to fit these values as a function of pressure. When applied to the present data it was found that the best fit that could be obtained was of the form

$$f(P) = \exp\left[A + \frac{B}{P} + \frac{C}{P^2}\right] \tag{5}$$

which on differentiation gives

$$\bar{V}_2 = \frac{B_1}{P^2} + \frac{C_1}{P^3} \tag{6}$$

The values of B_1 and C_1 at different temperatures are listed in Table II. Isothermal partial molar volumes as a function of pressure for four of these cases are shown in Figure 3. Similar curves are obtained for the rest. The values of $\bar{V}_2$ for naphthalene in naphthalene–CO_2 system obtained experimentally by Eckert et al. (*7*) have been compared with the values calculated according to eq 6. This is shown in Figure 4 and it is evident that there is excellent agreement.

The three isotherms for the partial molal volumes of dibenzothiophene cross over around 115 bar. Above this pressure the partial molal volumes decrease with increase in temperature ($\bar{V}[T_2] < \bar{V}[T_1]$; $T_2 > T_1$). This is because the vapor pressure increases faster than solubility with increase in temperature. Below this pressure, it is likely that one more crossover would have been noticed if the measurement were taken below 75 bar. Such phenomenon has been observed (for instance by Tsekhanskaya et al. (*9*) in their work on diphenylamine in CO_2 at 305.35 and 310.15 K) earlier, but has not been explained.

Conclusion

Solubility data for naphthalene, dibenzothiophene, and their mixture in supercritical carbon dioxide are presented. A method of calculating partial molar volumes from solubility data is suggested. By use of this method, the calculated partial molar volumes of naphthalene in naphthalene–CO_2 system are compared with the experimental partial molar volume data of Eckert et al. The agreement between experimental and calculated values is excellent.

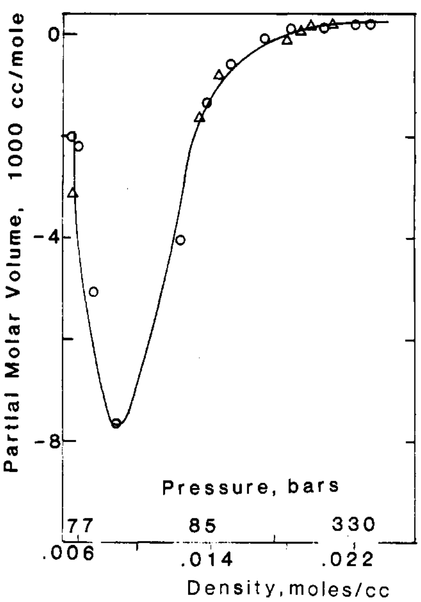

Figure 4. Comparison of calculated and experimental values of partial molar volume of naphthalene in CO_2; ○, experimental data of Eckert et al. (*7*); △, calculated values using eq 6.

Glossary

f_2	fugacity of solute, bar
P	pressure, bar
P_c	critical pressure of CO_2, bar
T	temperature, K
V_2^s	molar volume of solute, cm^3 mol^{-1}
V_2	partial molar volume, cm^3 mol^{-1}
γ_2	activity coefficient
X_2	mole fraction of solute
A, B, C	constants in eq 5
B_1, C_1	constants in eq 6
DBT	dibenzothiophene

Superscripts

f	fluid phase
s	solid phase

Subscripts

0	reference condition

Registry No. CO_2, 124-38-9; naphthalene, 91-20-3; dibenzothiophene, 132-65-0.

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