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Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide

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Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide were measured at various isotherms above 31.06 °C—the critical temperature of CO_2—and over a range of pressures from 80 to 500 atm. The upper critical end point for the naphthalene–carbon dioxide system is estimated from the solubility data to be 63 °C, 240 atm, and a naphthalene mole fraction of 0.16. The upper critical end-point temperature for the biphenyl–carbon dioxide system is ~56 °C and at a pressure near 460 atm. The biphenyl mole fraction at the upper critical end point (UCEP) is ~0.16.

Introduction

Solvent extraction with supercritical or near-critical fluids is the basis for several industrial extraction processes—such as deasphalting petroleum (*1*) and decaffeinating coffee (*2*)—and has recently been proposed as a method for deashing coal liquids (*3*) and for regenerating activated carbon (*4*). The recent development of supercritical-fluid chromatography is also based upon the enhanced solvent power of supercritical fluids and the ability to control solute elution through the column by varying the pressure of the mobile (supercritical) fluid phase in the vicinity of the critical region (*5*).

At present, thermodynamic formulations for correlating and predicting phase equilibrium behavior in the supercritical-fluid region are only semiquantitative, at best, because of a limited understanding of both the dense-fluid state in the critical region and theories of intermolecular interactions in multicomponent, highly asymmetric mixtures. Experimental solubility data in supercritical fluids—and particularly supercritical carbon dioxide (T_c = 31.06 °C, P_c = 72.86 atm)—are also scarce. Francis (*6*) has measured solubilities for a large number of solutes (including naphthalene and biphenyl) in liquid carbon dioxide near its critical point, but only at one temperature and pressure—saturated CO_2 at 25 °C. Tsekhanskaya et al. (*7*) measured solubilities of solid naphthalene in supercritical carbon dioxide at 35, 45, and 55 °C over a range of pressures up to 330 atm. The data illustrate the large solubility enhancement that occurs when compressing CO_2 to supercritical-fluid densities, and the dramatic sensitivity of solubilities to changes in fluid density near the critical point of the solvent. Their experimental results, however, do not include solubility behavior near the upper critical end point (UCEP) of the mixture. This UCEP for a binary mixture is depicted in Figure 1 and is defined by the intersection of the vapor–liquid critical curve (L = G) with the three-phase, solid–liquid–vapor curve (S_2LG). This phase behavior occurs for highly asymmetric mixtures where the limited solubility of the light component in the liquid phase of the nonvolatile component results in relatively small freezing-point depressions at elevated pressures. The UCEP temperature corresponds to the maximum temperature at which solid–vapor (or dense-fluid) equilibrium exists at all pressures. More importantly, the UCEP represents a mixture critical point in the presence of excess solid. The significance of this critical end point is illustrated in Figure 2, which shows experimental solubilities for solid naphthalene in supercritical ethylene at conditions near the UCEP of the binary mixture—T_{CM} = 52.1 °C and P_{CM} = 174 atm (*9*). At 50 °C, the solubility of naphthalene becomes very sensitive to changes in pressure and in temperature as the pressure approaches the UCEP pressure of 174 atm. (From standard thermodynamic relations at a mixture critical point, the 52.1 °C isotherm must have an inflection point at 174 atm and thus exhibit increased sensitivity of solubility to pressure and temperature.) This behavior is similar to the solubility enhancement that occurs at conditions near the critical point of the pure, supercritical-fluid solvent—ethylene. Solvent loadings, however, are about an order of magnitude greater near the UCEP than those near the critical point of pure ethylene (naphthalene mole fractions of 0.10–0.20 compared to 0.01–0.02). These results suggest that the region in the vicinity of the mixture critical point is of practical interest for supercritical-fluid solvent extractions. As part of our overall research program investigating phase equilibrium behavior in the supercritical-fluid region, we have measured solubilities of solid naphthalene and solid biphenyl in supercritical carbon dioxide over a range of temperatures and pressures from the critical point of pure CO_2 to the UCEP of the binary mixture.

Experimental Section

A schematic diagram of the experimental apparatus is presented in Figure 3. Liquid carbon dioxide (Linde "bone dry") at ambient temperatures is charged into an Altex high-pressure liquid pump (Altex Scientific, Inc. Model 100A) and compressed to the desired pressure. Constant flow rates ranging from 50 to 250 cm^3/min at STP are obtained at pressures up to 7400 psi. The pressure is typically maintained constant to better than ±1.0% of the desired value throughout an experiment. After reaching thermal equilibrium within the constant-temperature bath (controlled within ±0.15 °C with a Sargent-Welch Model ST Thermonitor), the solvent enters the first of two high-pressure equilibrium cells connected in series. Each cell (High-Pressure Equipment, Inc.) is ~46 cm in length with an internal volume of 32 cm^3 and is packed with a mixture of the heavy solute and 1-mm diameter glass beads. Glass wool plugs at the top of each column prevent entrainment of the condensed component. After exiting the second column, the saturated solution flows through a high-pressure switching valve (Valco Instruments Company) where a sample loop (~0.2 cm^3) can be isolated for analysis. The volume of carbon dioxide in the sample loop is determined to within ±0.3% by slowly expanding the CO_2 across a valve and displacing water. The sample loop is then flushed with a suitable solvent to recover the solid component. An internal standard is added to this solution, and the amount of the heavy solute present is determined by using standard gas-chromatographic techniques. Analyses on each sample are accomplished in triplicate with a standard deviation generally less than ±0.7%. The continuous stream exiting the switching valve is flashed across a heated metering valve (Autoclave Engineers, Inc.), and the heavy solute is collected in a cold trap held at ice temperature. Gaseous carbon dioxide is subsequently passed through a bubble meter to determine flow rate.

The equilibrium temperature and pressure of the system are measured at the exit of the second equilibrium cell. Pressure measurement is accomplished by using a Bourdon-type Heise gauge (Gregory Company Model CM) with a range of 0–10 000 psi and an accuracy of ±10 psi. Temperature is measured with an accuracy of ±0.15 °C by using a platinum resistance

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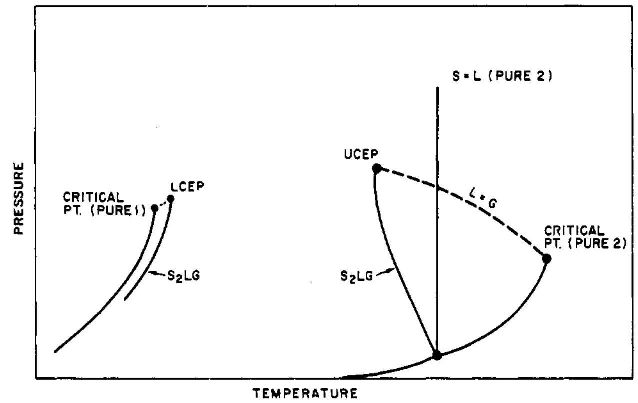

Figure 1. Pressure-temperature diagram for a highly asymmetric binary mixture (*8*).

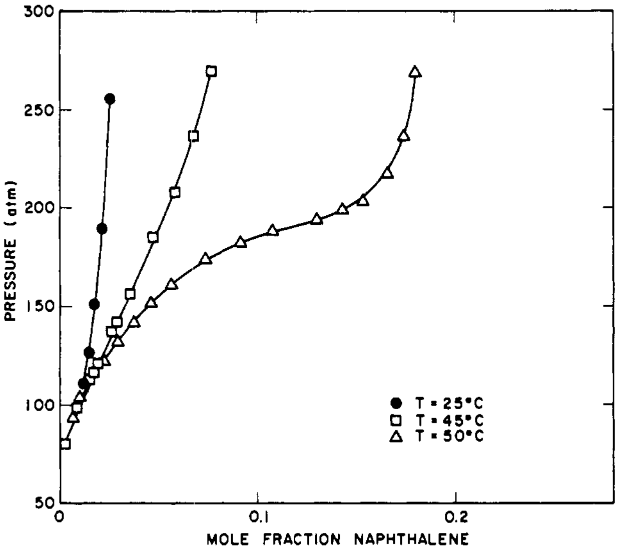

Figure 2. Experimental solubilities for solid naphthalene in supercritical ethylene near the UCEP of the binary mixture (*9*).

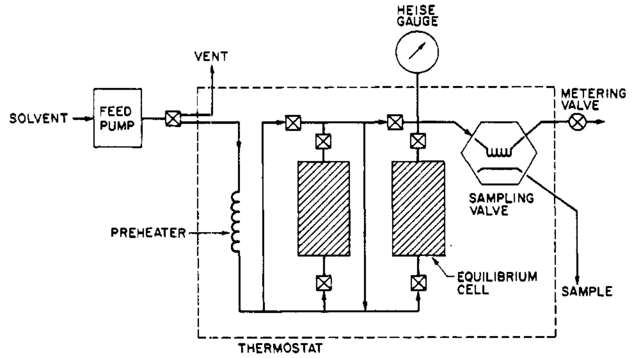

Figure 3. Schematic diagram of the experimental apparatus for measuring solubilities.

thermometer (Engelhard Industries) calibrated on the 1968 IPTS scale.

The naphthalene, supplied by Fisher Scientific Company, was Fisher Certified grade (99+% purity). The biphenyl, supplied by Aldrich Chemical Company, was 99+% pure. The stated purity of both chemicals was verified by gas-chromatographic analysis and subsequently used without further purification.

Results

The experimental solubility data for solid naphthalene in supercritical carbon dioxide at 35.0, 55.0, 60.4, and 64.9 °C are presented in Table I, and the data for solid biphenyl in supercritical CO_2 at 35.8, 45.4, 49.5, 55.2, and 57.5 °C are given in Table II. The reported mole fractions represent an average value of at least three independent measurements reproducible to better than 3% and have an average experimental error of ±0.7%. The naphthalene and biphenyl solubilities are also plotted in Figures 4 and 5, respectively.

For the naphthalene-carbon dioxide system, our results agree to better than 2-4% with the solubility data of Tsekhanskaya

Table I. Experimental Solubilities for Naphthalene in Supercritical Carbon Dioxide

press., atm	naphthalene mole fraction	press., atm	naphthalene mole fraction
$T = 35.0$ °C		$T = 60.4$ °C	
85.7	0.00750	107.0	0.005238
96.9	0.00975	132.1	0.01516
105.1	0.01066	150.5	0.02589
131.3	0.01410	162.1	0.03401
166.8	0.01605	173.3	0.04296
196.9	0.01709	181.3	0.04436
219.5	0.01830	190.1	0.05386
239.3	0.01908	201.3	0.05903
252.0	0.01922	203.4	0.06259
$T = 55.0$ °C		214.2	0.06963
81.1	0.001313	214.6	0.06990
91.1	0.001672	223.6	0.07720
101.0	0.002920	228.9	0.07721
108.3	0.005464	232.8	0.08306
120.1	0.01229	244.9	0.09064
131.5	0.02114	251.7	0.09204
141.8	0.02544	254.4	0.09583
158.5	0.03053	269.7	0.09756
169.4	0.03387	287.6	0.09802
172.6	0.03473	$T = 64.9$ °C	
187.1	0.03928	149.8	0.02427
207.6	0.04224	169.4	0.03765
220.6	0.04366	182.8	0.04428
234.7	0.04586	189.8	0.05015
248.3	0.04969	210.2	0.06440
284.0	0.05382	222.1	0.07309
		229.2	0.07902
		236.5	(0.3206)
		252.7	(0.3237)
		271.4	(0.2999)

Table II. Experimental Solubilities for Biphenyl in Supercritical Carbon Dioxide

press., atm	biphenyl mole fraction	press., atm	biphenyl mole fraction
$T = 35.8$ °C		$T = 55.2$ °C	
104.6	0.01043	109.2	0.004474
126.2	0.01077	130.9	0.01031
165.1	0.01296	151.7	0.01481
201.7	0.01431	165.1	0.01829
239.1	0.01536	205.9	0.02478
297.3	0.01546	228.6	0.03251
353.4	0.01586	249.3	0.03516
435.4	0.01541	292.7	0.04398
$T = 45.4$ °C		330.3	0.05615
151.5	0.01556	381.6	0.06862
178.9	0.01959	407.5	0.07918
206.8	0.02210	438.1	0.09775
235.7	0.02415	463.9	0.11054
264.6	0.02561	476.5	0.12669
325.8	0.02738	484.0	0.18165
374.5	0.02751	$T = 57.5$ °C	
442.5	0.02722	356.8	0.06365
$T = 49.5$ °C		396.9	0.07563
153.6	0.01782	424.8	0.09208
201.9	0.02689	443.5	(0.19798)
236.0	0.03124		
292.7	0.03605		
332.6	0.03764		
374.5	0.03795		
417.0	0.03765		
469.0	0.03605		

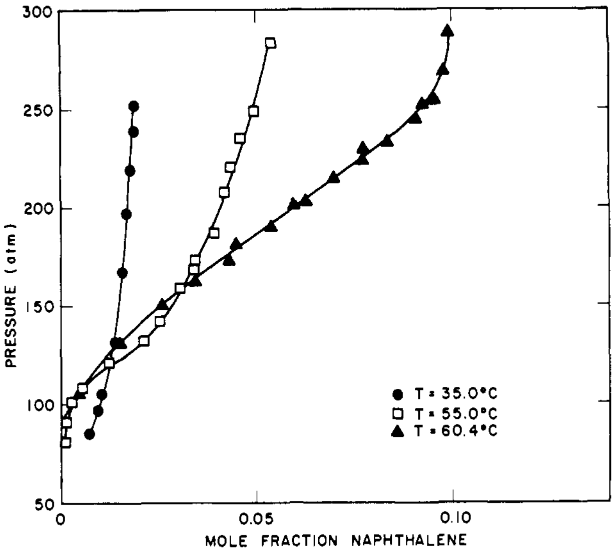

Figure 4. Experimental solubilities for solid naphthalene in supercritical carbon dioxide at 35.0, 55.0, and 60.4 °C.

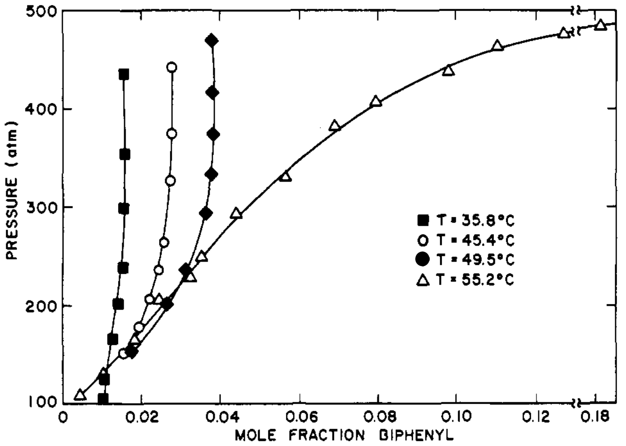

Figure 5. Experimental solubilities for solid biphenyl in supercritical carbon dioxide at 35.8, 45.4, 49.5, and 55.2 °C.

et al. (*7*) at 35 and 55 °C over the entire pressure range. The 35 °C isotherm for this system is characteristic of solid solubility behavior at temperatures near the critical temperature of the supercritical-fluid solvent. At this temperature, large (e.g., several orders of magnitude) changes in solubility occur for relatively small changes in pressure around the critical pressure of the solvent; however, the limiting (maximum) solubility at elevated pressures is comparatively modest—in this case, the naphthalene mole fraction approaches 0.02. Solubility behavior near the critical point of CO_2 is clearly illustrated if the logarithm of solubility is plotted vs. pressure at 35 °C (*10*). The 55 °C isotherm exhibits essentially the same behavior—the changes in solubility with pressure near the critical point of CO_2 are somewhat less dramatic, but the limiting or maximum solubility at elevated pressures is greater than that at 35 °C. For the 60.4 °C isotherm, however, solubilities at elevated pressures are significantly enhanced (about a factor of 2 greater than those at 55 °C) with relatively small changes in temperature. These results are similar to the observations of Diepen and Scheffer for naphthalene–ethylene shown in Figure 2 and suggest that 60.4 °C is near the UCEP temperature for the naphthalene–CO_2 system. Our solubility data at 64.9 °C (presented in Table I only) also support this conclusion. At this temperature and pressures below 236 atm, naphthalene solubilities are comparable to those at 60.4 °C; however, at higher pressures, samples were obtained with naphthalene mole fractions greater than 0.3. This behavior indicates that the solid–liquid–vapor curve had been intersected at conditions close to the UCEP, and the mole fractions in parentheses in Table I (corresponding to the maximum solubilities observed) represent compositions of the liquid phase on the three-phase curve. These observations are also in agreement with the experimental results of Büchner (*11*), who observed for naphthalene–CO_2 the formation of a third (liquid) phase at 64 °C and elevated pressures (values were not given) with a naphthalene mole fraction of 0.28. Our experimental results indicate that the UCEP temperature is between 60.4 and 64.9 °C and that the UCEP pressure is slightly above 236 atm. We consider a good estimate of the UCEP for naphthalene–CO_2 to be 63 °C, 240 atm, and a naphthalene mole fraction of ~0.16. This compares with the UCEP for naphthalene–ethylene of 52.1 °C, 174 atm, and a naphthalene mole fraction of 0.17 (*9*).

The solubilities of biphenyl in supercritical carbon dioxide are somewhat less than those for naphthalene, which is in agreement with the experimental results of Francis (*6*) for solubilities in liquid CO_2 at 25 °C. The isotherms at 35.8, 45.4, and 49.4 °C are similar to those at 35 and 55 °C for naphthalene–carbon dioxide. The 55.2 °C isotherm begins to show a solubility enhancement characteristic of behavior near the UCEP, and solubilities at 57.5 °C (given in Table II) exhibit behavior comparable to that for naphthalene–CO_2 at 64.9 °C. This implies that the UCEP temperature for biphenyl–CO_2 is between 55.2 and 57.5 °C. A UCEP temperature for biphenyl–CO_2 lower than that obtained for naphthalene–CO_2 would be expected on the basis of the difference in melting points for the two pure solids—naphthalene melts at 80.4 °C and biphenyl melts at 69.3 °C. The UCEP pressure for biphenyl–CO_2 is appreciably higher than that estimated for naphthalene–CO_2 as indicated by the solubility behavior at 55.2 and 57.5 °C. A reasonable approximation of the UCEP temperature and pressure for biphenyl–CO_2 would be 56 °C and 460 atm. The biphenyl mole fraction at the UCEP appears to be about the same as was estimated for naphthalene–CO_2.

It is interesting to note the solubility behavior at high pressures for the 49.5 °C isotherm. As pressure increases, the measured solubility of naphthalene increases until a maximum is reached at ~375 atm. At this point solubility decreases with increasing pressure. This behavior is a free-volume effect which results from the large size disparity between biphenyl and CO_2 (*12*). Solubility measurements at higher pressures should reveal the same behavior for the other isotherms. However, measurements were not accomplished above 500 atm, which is the maximum pressure that can be obtained with the present experimental setup.

The solubility behavior near the UCEP for solid–supercritical fluid systems has interesting practical implications. The solvent power of the fluid in this region is appreciably greater than in the region near the pure-component critical point for the fluid, while solubilities remain comparably sensitive to pressure and temperature changes in both regions. There is, however, a large disparity in the pressure required to operate near the UCEP depending on the constituents involved—174 atm for naphthalene–ethylene, 240 atm for naphthalene–carbon dioxide, and 460 atm for biphenyl–carbon dioxide. Since it would be advantageous to predict the UCEP conditions from an accurate thermodynamic model, the relatively meager experimental data base for this phase equilibrium behavior needs to be significantly extended.

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Vapor–Liquid Equilibria for the System *n*-Heptane–*o*-Xylene at 348.1, 358.1, and 368.3 K

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Isothermal vapor–liquid equilibrium data for the *n*-heptane–*o*-xylene system have been determined at 348.1, 358.1, and 368.3 K in a modified Fowler–Norris cell. The data have been correlated by using Barker's method together with the four-suffix Margules equation.

Introduction

A survey of the vapor–liquid equilibrium data compilation by Wichterle et al. (*8*), and of the more recent literature, revealed that the *n*-heptane–*o*-xylene system has not been investigated. Wichterle (*7*) and Michishita et al. (*5*) report data for the *n*-heptane–*p*-xylene system at 90 °C and 760 mmHg, respectively.

Mixtures of paraffinic and aromatic hydrocarbons are important from a theoretical and a practical viewpoint. Accordingly, the equilibrium pressures and phase compositions for the *n*-heptane–*o*-xylene system were measured under isothermal conditions of 348.1, 358.1, and 368.3 K.

Experimental Section

The reagents used were manufactured by Hopkin & Williams, Ltd. (England), and were AnalaR (pro-analysi) grade. They were further purified by distillation in a 20-plate Oldershaw column, operated at a high reflux rate, and from which heart cuts were collected. The physical properties of the two components, together with the corresponding literature values, are listed in Table I.

The equilibrium apparatus was a modified Fowler–Norris cell (*3*), in which both phases are recirculated. It is described by Kesselman et al. (*4*). The two Teflon sampling plugs had a narrow perforation covered by a rubber septum held in place by a special brass screw. Samples were withdrawn with hypodermic syringes after puncturing the septum.

The cell was connected to a constant-pressure system consisting of a cartesian manostat, a mercury manometer, which could be read to within ±0.013 kPa (0.1 mmHg), a 5 × 10^{-3} m^3 ballast flask, a vacuum pump, and a regulated supply of dry air.

The equilibrium temperature was measured to within ±0.1 K with certified mercury thermometers.

Composition of the coexisting phases was determined by measuring the refractive index at 25 °C. Previously, this property was measured for mixtures of known composition and was correlated, within experimental uncertainty, by the equation

$$n_D(x_1) = 1.3850x_1 + 1.5025x_2 - \frac{x_1x_2}{50.8397 - 14.6474x_1} \quad (1)$$

Table I. Physical Properties of the Pure Components

	n-heptane		*o*-xylene	
	exptl	lit.[a]	exptl	lit.[a]
density, g/cm³ (20 °C)	0.6839	0.68376	0.8800	0.88020
refractive index (25 °C)	1.3850	1.38511	1.5025	1.50295
vapor pressure, kPa				
348.1 K	47.96	48.02	10.22	10.31
358.1 K	66.93	66.90	15.30	15.30
368.3 K	91.98	91.81	22.19	22.29

[a] Reference 1.

The refractive index was read to within ±0.0001 units.

The estimated experimental uncertainties are as follows: temperature ±0.1 K; pressure ±0.067 kPa; composition ±0.005 mole fraction.

Results

Experimental temperatures, pressures, and liquid- and vapor-phase mole fractions of *n*-heptane are reported in Table II and shown graphically in Figure 1.

Correlation of the Data and Discussion

In order to smooth the experimental data and get an indirect check of their thermodynamic consistency, we used the method proposed by Barker (*2*). On the assumption that the excess Gibbs free energy of the mixture was represented by the four-suffix Margules equation

$$g = G^E/RT = x_1x_2(A_{21}x_1 + A_{12}x_2 - Dx_1x_2) \quad (2)$$

equilibrium pressures were calculated as

$$P = \frac{x_1\varphi_1{}^sP_1{}^s}{\varphi_1}\exp\left[\frac{v_1{}^L}{RT}(P - P_1{}^s)\right]\exp\left(g + x_2\frac{dg}{dx_1}\right) + \frac{x_2\varphi_2{}^sP_2{}^s}{\varphi_2}\exp\left[\frac{v_2{}^L}{RT}(P - P_2{}^s)\right]\exp\left(g - x_1\frac{dg}{dx_1}\right) \quad (3)$$

The vapor pressures were the experimental values.

Vapor-phase fugacity coefficients φ_i and $\varphi_i{}^s$ were calculated from the virial equation of state, truncated after the second virial coefficient. Pure-component and interaction second virial coefficients were obtained from the generalized correlation of Tsonopoulos (*6*). Liquid volumes were taken from ref 1. All these quantities are listed in Table III.

Using a nonlinear least-squares regression scheme, which minimized the deviations between calculated and experimental

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