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# Density Changes in Supercritical Solvent + Hydrocarbon Solute Binary Mixtures

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In this work, densities of supercritical carbon dioxide and ethane containing naphthalene and octacosane were measured with a high-pressure vibrating tube densitometer. The measurements were carried out at temperatures of 308.2 and 318.2 K and pressures up to 20 MPa. A single-pass flow system is used in which the solid solute is continuously extracted with the supercritical fluid. The concentration of the extracted solute in the mixture is determined by depressurizing the solution and dissolving the solute in toluene. Densities were obtained for both saturated and unsaturated mixtures. Solubility and density data were obtained for the system carbon dioxide + naphthalene and compared to literature data. In addition, data were obtained for the systems carbon dioxide + octacosane and ethane + octacosane. The densities obtained were correlated using the Peng−Robinson equation of state to within 5% standard error.

## Introduction

In recent years supercritical fluid extraction (SFE) is increasingly being considered as an alternative to conventional separation techniques. Although supercritical fluids (SFs) have been used for a variety of industrial applications, there is still a need for fundamental research to understand the complicated phase behavior and solution phenomena of these high-pressure solvents. A number of studies have focused on the experimental determination of solubilities of model hydrocarbon solutes like naphthalene and octacosane in supercritical fluids including carbon dioxide and ethane (Tsekhanskaya et al., 1964; McHugh et al., 1984; Reverchon et al., 1993; Moradinia and Teja, 1986; Suleiman and Eckert, 1995; Kalaga and Trebble, 1997). Substantially fewer investigations have been carried out in the area of the volumetric behavior of these mixtures (Tsekhanskaya et al., 1966; McHugh et al., 1984; Eckert et al., 1983; Eckert et al., 1986).

In this work, the densities of binary mixtures of supercritical carbon dioxide + naphthalene, carbon dioxide + octacosane, and ethane + octacosane have been measured using a flow apparatus. The densities were obtained for saturated and unsaturated mixtures for pressures from 6.9 to 20 MPa and temperatures of 308.2 and 318.2 K using a vibrating tube densitometer. This mixture volume data provide information about the excess volumes and the solute partial molar volumes which can be used to analyze supercritical solution phenomena. In addition, this volumetric data can be used to evaluate the correlational and predictive capabilities of equations of state and other thermodynamic models (Eckert et al., 1983). With the mixture volume data and a suitable model, density measurements could also be used in place of composition measurements, thus eliminating the problem of sampling high-pressure fluids.

## Experimental Section

A schematic diagram of the experimental apparatus is presented in Figure 1. The apparatus is similar to that described previously by Kalaga and Trebble (1997). In this work, the constant-temperature bath was replaced by a convection oven and a densitometer was installed at the extractor exit.

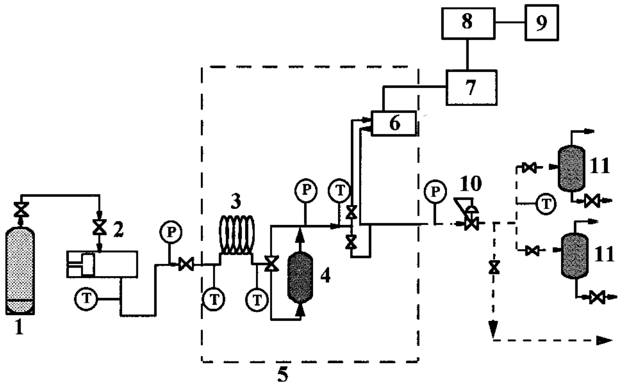

**Figure 1.** Schematic diagram of the experimental apparatus: (1) solvent cylinder; (2) Ruska pump; (3) preheater coil; (4) extractor; (5) temperature-controlled oven; (6) densitometer remote cell; (7) densitometer controller; (8) densitometer indicator; (9) density recorder; (10) micrometering valve; (11) toluene baths; (P) pressure transducer; (T) thermocouple.

Carbon dioxide and ethane were withdrawn as liquids from the solvent cylinder into the Ruska pump and were compressed to the desired pressure. The Ruska pump was equipped with a geared motor, which allowed the pumping of the solvent at required flow rates. These high-pressure solvents were then sent to a preheater coil (9.15 m long and 0.0064 m diameter), where the solvent reached the desired temperature. The pure solvents were then passed through the extractor. The extractor, which was 0.3 m in length and 0.02 m in diameter, was packed with powdered solute. The extractor was fitted with glass beads at the entrance and glass wool at the exit to minimize entrance effects and entrainment. The temperatures of the solvent entering the extractor and the mixture leaving the extractor were monitored with T type thermocouples calibrated against a platinum resistance thermometer traceable to NIST standards. The pressure at the exit of the extractor

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is monitored using an absolute pressure transducer (Rosemount 3051CA). The mixture from the extractor was then passed through the vibrating tube of the densitometer. The preheater, the extractor, and the vibrating tube were placed inside a temperature-controlled oven. The oven was a Blue M convection oven equipped with a Watlow PID temperature controller. The vibrating tube was controlled by using the remote cell (Anton Paar DMA 512), and the output of the remote cell was sent to another densitometer (AP DMA 48) which converts the period of oscillation into density and displays the same. The output of the DMA 48 was then sent to a data acquisition system for dynamic density measurement.

The compositional analysis of the mixture was done using the sampling technique described previously (Kalaga and Trebble, 1997) whereby the high-pressure mixture was depressurized across a micrometering valve and passed through a bath containing toluene. The toluene with the dissolved solute was then analyzed in a gas chromatograph equipped with a flame ionization detector. The concentration of the solute in the mixture was then calculated from the amount of solvent pumped through the extractor, obtained from the conditions at the pump. To avoid precipitation of the solid due to expansion, the entire line from the exit of the oven to the toluene bath was heat traced. The temperature of this line was maintained over 400 K. The sampling was performed over fixed time intervals ranging from 10 min to 1 h by switching the three-way valve to the sampling bath. During this sampling period the temperatures, pressures, and density were recorded using a data acquisition system.

The pressure was controlled to within 70 KPa, and the temperature was controlled to within 0.06 K. Due to these fluctuations the density was constant to within 1 kg/m$^3$. Saturated solutions were obtained by pumping the solvent at a low enough flow rate through the extractor. At flow rates between 25 × $10^{-6}$ and 100 × $10^{-6}$ m$^3$/h at pump conditions, it was found that the concentration of the solute was independent of flow rate, indicating that the solution was saturated. Unsaturated solutions were obtained by pumping the solvent at much higher flow rates ranging from 280 × $10^{-6}$ to 800 × $10^{-6}$ m$^3$/h.

***Source and Purity of Materials.*** The solutes naphthalene and octacosane used in this work were obtained from Aldrich Chemical Co. and were used without further purification. The stated purity of octacosane and naphthalene was over 99%. The solvents carbon dioxide and ethane obtained from Praxair were of CP grade with over 99% purity. The toluene used for dissolving the solid was OmniSolv grade, suitable for chromatography with over 99.99% assay.

## Results and Discussion

The densitometer was calibrated using the pure carbon dioxide densities obtained from the NIST Thermophysical Properties of Pure Fluids Database (version 3.1). The calibration was done at two pressures for each temperature. The pure solvent densities obtained at other pressures were within 0.2% of the NIST values. The concentration (mole fraction solid) and density data for the system carbon dioxide + naphthalene are presented in Table 1 for the temperatures 308.2 and 318.2 K. The carbon dioxide + naphthalene system was chosen because of the previously published data (Tsekhanskaya et al., 1964, 1966). Duplicate and triplicate measurements showed repeatability to within 2% in solubility and 1% in density. The tabulated values represent the average values of these measurements. Also, the method of dynamic sampling (collecting small samples every 15 min for 1 h) showed that the amount of the solute in the toluene bath increased linearly with time, indicating that there was no precipitation in the apparatus.

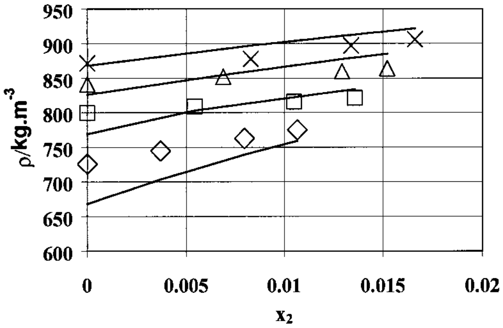

**Figure 2.** Density of carbon dioxide (1) + naphthalene (2) at 308.2 K: (×) 20.7 MPa; (△) 17.2 MPa; (□) 13.8 MPa; (◇) 10.3 MPa; (—) PR EOS.

**Table 1. Density Data for Carbon Dioxide (1) + Naphthalene (2) Mixtures**

| equilibrium data | | | non-equilibrium data | | |
|---|---|---|---|---|---|
| $P$/MPa | $10^3x_2$ | $\rho$/kg·m$^{-3}$ | $P$/MPa | $10^3x_2$ | $\rho$/kg·m$^{-3}$ |
| | | $T$ = 308.2 K | | | |
| *9.13* | *8.30* | *706* | 9.65 | 5.41 | 727 |
| *10.43* | *10.66* | *775* | 10.41 | 7.97 | 762 |
| *13.82* | *13.59* | *820* | 13.77 | 10.50 | 815 |
| *17.28* | *15.21* | *864* | 17.29 | 12.93 | 860 |
| *20.69* | *16.61* | *881* | 20.65 | 13.39 | 880 |
| | | | 10.38 | 3.70 | 745 |
| | | | 13.81 | 5.43 | 808 |
| | | | 17.27 | 6.88 | 852 |
| | | | 20.65 | 8.29 | 878 |
| | | $T$ = 318.2 K | | | |
| *10.31* | *8.43* | *632* | 10.36 | 6.43 | 628 |
| *13.79* | *17.62* | *785* | 13.87 | 14.49 | 775 |
| *17.20* | *22.33* | *821* | 17.27 | 19.11 | 815 |
| *20.69* | *24.89* | *869* | 20.68 | 22.34 | 864 |
| | | | 10.42 | 4.92 | 622 |
| | | | 13.75 | 10.78 | 768 |
| | | | 17.18 | 14.75 | 808 |
| | | | 20.71 | 17.32 | 855 |
| | | | 10.35 | 2.25 | 594 |
| | | | 13.78 | 5.12 | 752 |
| | | | 17.26 | 7.94 | 793 |
| | | | 20.75 | 9.34 | 841 |

The data from Table 1 for carbon dioxide + naphthalene at 308.2 K are plotted in Figure 2. The left ends of the curves represent the pure solvent density, and the right ends represent the density at saturation. It can be seen that the variation of density with concentration is more significant at lower pressures. The densities obtained were correlated using the Peng–Robinson equation of state (PR EOS) (Peng and Robinson, 1976) with the following mixing rules:

$$(a\alpha)_{\mathrm{m}} = \sum_i \sum_j y_i y_j (1 - k_{ij})(a_i \alpha_i a_j \alpha_j)^{0.5}$$

$$b_{\mathrm{m}} = \sum_i y_i b_i$$

For the case of carbon dioxide + naphthalene the PR EOS was able to correlate the entire data set to within 3% average absolute relative deviation (AARD). Only one adjustable parameter $k_{ij}$ was used to fit the data. The interaction parameter $k_{ij}$ was obtained by minimizing the error between experimental and calculated values of density. The results of the modeling are shown in Table 4.

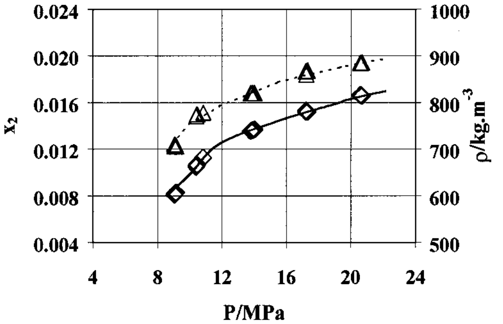

**Figure 3.** Solubility and density of carbon dioxide (1) + naphthalene (2) at 308.2 K: (◇) solubility (this work); (—) solubility (Tsekhanskaya et al., 1966); (△) density (this work); (- - -) density (Tsekhanskaya et al., 1966).

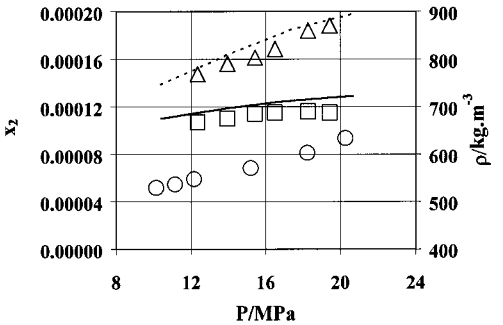

**Figure 4.** Solubility and density of carbon dioxide (1) + octacosane (2) at 308.2 K: (—) solubility (this work); (□) solubility (McHugh et al., 1984*); (○) solubility (Reverchon et al., 1993); (- - -) density (this work); (△) density (McHugh et al., 1984*); * denotes data at 307.9 K.

**Table 2. Density Data for a Carbon Dioxide (1) + Octacosane (2) Mixture at 308.2 K**

| equilibrium data | | |
|---|---|---|
| *P*/MPa | $10^3 x_2$ | ρ/kg·m$^{-3}$ |
| 10.39 | 11.00 | 747 |
| 13.82 | 11.85 | 807 |
| 17.30 | 12.50 | 861 |
| 20.67 | 12.90 | 895 |

It was found that there is only a marginal improvement in the performance of the model by considering $k_{ij}$ to be temperature dependent. Hence, $k_{ij}$ was forced to be independent of temperature and the predictions were within 2.5% for 308.2 K and 3.5% for 318.2 K. The model predictions are shown in Figure 2 (solid lines) along with the experimental data (symbols).

Direct comparison with other data is not possible on these graphs due to different pressures and concentrations used in the different studies. Hence, a comparison of the equilibrium data (solubility and density) at 308.2 K with previously published data (Tsekhanskaya et al., 1966) is made in Figure 3. It can be seen that there is excellent agreement between the two sets of data. Similar agreement was found for solubility data at 318.2 K. The data obtained from repeatability tests are also shown in the figure.

Saturation data were also obtained for the system carbon dioxide + octacosane and are shown in Table 2 and Figure 4. As can be seen from the graph, there is a large discrepancy in the solubility data between this work and that of Reverchon et al. (1993), whereas the data of McHugh et al. (1984) agree closely with this work. There is also a slight difference in the densities obtained at saturation between this work and that of McHugh et al. (1984). These differences in solubilities and densities between this work and that of McHugh et al. (1984) may be partly attributed to the fact that there is a difference of 0.3 K between both works. The solubilities in this system are 2 orders of magnitude lower than those for the carbon dioxide + naphthalene system. Because of the low solubilities, the amount of solid extracted is very low. If the experimental method is limited by the amount of solvent that can be sampled, it may lead to concentrations close to or within the lower limits measurable with the apparatus. The apparatus used by McHugh et al. (1984) had a fixed volume ($0.2092 \times 10^{-6}$ m$^3$) in the sampling loop which was flushed with toluene to obtain the concentration of the solid. This would severely limit the amount of solid collected in the loop. The method used by Reverchon et al. (1993) obtained the solubilities by collecting the solid in Pyrex tubes packed with glass wool, immersed in a cold bath. Again, to obtain an accurate gravimetric solubility value, large amounts of solid would be required.

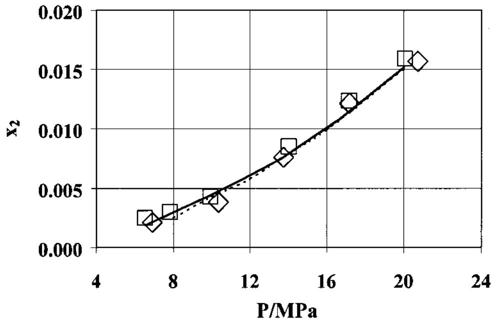

**Figure 5.** Solubility of octacosane (2) in ethane (1) at 308.2 K: (◇) solubility (this work); (—) solubility (Moradinia and Teja, 1986); (□) solubility (Kalaga and Trebble, 1997); (- - -) solubility (Suleiman and Eckert, 1994).

The technique of sampling by dissolving the solute in an organic solvent from a flowing system leads to better accuracy for compositional analysis, as it provides flexibility in terms of the amount of solvent pumped and also the amount of organic solvent in the bath. In this work the experiments were designed in such a way that at least 100 mg of solid was extracted, providing at least a 1 wt % dissolution in 10 g of toluene. Duplicate measurements showed repeatability within 2%.

For measuring the densities of the system ethane + octacosane, the densitometer was calibrated against pure ethane, with the densities obtained from the NIST property database. The pure solvent densities obtained were within 0.2% of the NIST values. The mixture densities were repeatable to better than 1%, and the solubility data from duplicate and triplicate measurements were reproducible to within 4% at lower pressures and 2% at higher pressures. There is solubility information available (Moradinia and Teja, 1986; Suleiman and Eckert, 1995; Kalaga and Trebble, 1997) for the system ethane + octacosane in the literature. The solubility data for 308.2 K are plotted in Figure 5 as a function of pressure.

It can be seen from Figure 5 that there is good agreement between all the sets of data. Similar agreement was found between the data of Suleiman and Eckert (1995) and this work at 318.2 K. Although there are published solubility data, there is no available information on densities or volumes for this system. The experimental data obtained in this work for saturated and unsaturated densities for the system ethane + octacosane are presented in Table 3.

The variation of density with mole fraction of octacosane is shown in Figure 6 for 318.2 K. Again, the leftmost points represent pure solvent density, and the rightmost, the

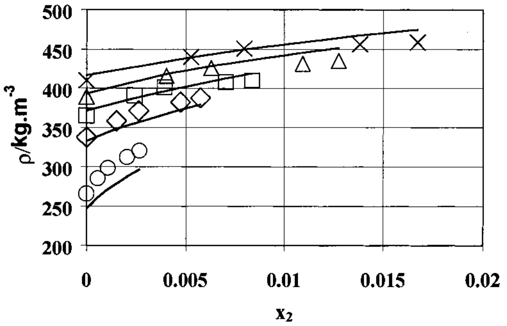

**Figure 6.** Density of ethane (1) + octacosane (2) at 318.2 K: (×) 20.7 MPa; (△) 17.2 MPa; (□) 13.8 MPa; (◇) 10.3 MPa; (○) 6.9 MPa; (—) PR EOS.

**Table 3. Density Data for Ethane (1) + Octacosane (2) Mixtures**

| equilibrium data | | | non-equilibrium data | | |
|---|---|---|---|---|---|
| $P$/MPa | $10^3x_2$ | $\rho$/kg·m$^{-3}$ | $P$/MPa | $10^3x_2$ | $\rho$/kg·m$^{-3}$ |
| | | $T = 308.2$ K | | | |
| *6.90* | *2.12* | *365* | 6.89 | 1.72 | 362 |
| *10.40* | *4.14* | *398* | 10.39 | 3.11 | 396 |
| *13.76* | *7.62* | *414* | 13.76 | 6.40 | 412 |
| *17.29* | *12.16* | *426* | 17.26 | 10.11 | 423 |
| *20.72* | *15.67* | *438* | 20.75 | 14.12 | 437 |
| | | | 6.95 | 0.86 | 355 |
| | | | 10.29 | 1.63 | 390 |
| | | | 13.78 | 3.39 | 407 |
| | | | 17.26 | 5.34 | 418 |
| | | | 20.66 | 7.85 | 434 |
| | | | 6.91 | 0.40 | 345 |
| | | | 10.40 | 0.82 | 382 |
| | | | 13.86 | 1.77 | 402 |
| | | | 17.32 | 2.90 | 412 |
| | | | 20.69 | 4.24 | 432 |
| | | $T = 318.2$ K | | | |
| *6.91* | *2.66* | *320* | 6.93 | 2.03 | 312 |
| *10.36* | *5.74* | *387* | 10.38 | 4.73 | 382 |
| *13.85* | *8.35* | *419* | 13.86 | 7.03 | 407 |
| *17.23* | *12.75* | *435* | 17.23 | 10.93 | 431 |
| *20.69* | *16.72* | *458* | 20.65 | 13.82 | 456 |
| | | | 6.90 | 1.07 | 298 |
| | | | 10.41 | 2.62 | 371 |
| | | | 13.79 | 3.93 | 400 |
| | | | 17.26 | 6.28 | 425 |
| | | | 20.75 | 7.96 | 450 |
| | | | 6.95 | 0.56 | 285 |
| | | | 10.28 | 1.51 | 358 |
| | | | 13.78 | 2.42 | 390 |
| | | | 17.28 | 4.02 | 415 |
| | | | 20.65 | 5.26 | 440 |

density at saturation. The lower pressure data are a stronger function of the solute concentration as compared to those for higher pressures. The predictions from PR EOS are also shown in the figure, and the correlation of the entire data set was within 4.5% AARD.

It can be seen from Figures 2 and 6 that the predictions from the EOS are poor at lower pressures where the solvent is near the critical point, which is to be expected from any two-parameter EOS with a fixed critical compressibility. The results of the modeling of the densities with PR EOS are summarized in Table 4. The critical properties for the pure components are obtained from DIPPR and NIST fluid property databases and are presented in Table 5.

**Table 4. PR EOS Modeling**

| system | $k_{ij}$ | % AARD |
|---|---|---|
| carbon dioxide + naphthalene | −0.15 | 3.0 |
| carbon dioxide + octacosane | −0.59 | 4.9 |
| ethane + octacosane | −0.35 | 4.5 |

**Table 5. Critical Properties Used**

| component | $T_c$/K | $P_c$/MPa | $\omega$ |
|---|---|---|---|
| carbon dioxide | 304.1 | 7.38 | 0.239 |
| ethane | 305.4 | 4.88 | 0.099 |
| naphthalene | 748.3 | 4.051 | 0.302 |
| octacosane | 843.0 | 0.888 | 1.1446 |

## Conclusions

It was demonstrated that reliable density or volume data for supercritical fluid + hydrocarbon solute systems could be easily obtained by using a conventional flow method along with a densitometer. It was found that density is a stronger function of the solute concentration at low pressures compared to high pressures. It is possible to represent the densities of these supercritical solvent + hydrocarbon solute systems with a simple PR EOS to within 5% AARD using only one adjustable parameter.

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