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Solubilities of Tetracosane, Octacosane, and Dotriacontane in Supercritical Ethane

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The solubilities of tetracosane, octacosane, and dotriacontane in ethane were determined at a temperature of 308.15 K and at pressures ranging from 50 bar to 200 bar. A dynamic single-pass flow system was used for this purpose. The extracted solute was dissolved in toluene after depressurizing the supercritical mixture. This method of measuring the solubilities facilitates the collection of dynamic solubility data since the concentration of solute in toluene can be determined as the experiment proceeds. Dynamic sampling provides more reliable and accurate solubility information compared to the conventional methods based on the weight of solute extracted. The experimental solubilities measured in this work are in agreement with most of the previously published data. The solubilities obtained in this work were modeled using the translated Trebble−Bishnoi−Salim (TBS) EOS which correlated the solubility data successfully to within an average error of 6% for all the systems studied.

Introduction

Supercritical fluids (SCFs) are solvents with many unique properties. The strong ability of SCFs to attract low-volatility materials from various mixtures has made supercritical fluid extraction (SFE) a viable alternative to conventional separation processes (Paulaitis et al., 1983) and also an effective tool for enhanced oil recovery (EOR) processes (Eisenbach et al., 1983; Orr et al., 1981, 1983; Deo et al., 1992). At the center of this technology lies the enhanced solubility of the solute in the supercritical solvent, and this is the most important thermophysical property that must be determined and modeled for any SFE process design.

High molecular weight *n*-paraffins can be used as model compounds for petroleum industry applications as they comprise the majority of the compounds found in crude oils. With respect to these applications, the solubilities of some *n*-paraffins in supercritical carbon dioxide and ethane have been reported in the literature (McHugh et al., 1984; Moradinia and Teja, 1987; Suleiman and Eckert, 1995). In this work, equilibrium solubility measurements for tetracosane, octacosane, and dotriacontane in supercritical ethane are reported at 308.15 K and at pressures ranging from 50 bar to 200 bar.

Experimental Section

A schematic diagram of the experimental single pass flow apparatus is presented in Figure 1. The apparatus is similar to those described by various researchers for measuring supercritical fluid solubilities (McHugh and Paulaitis, 1980; Kurnik et al., 1981). This work differs from other mentioned works in the sampling method used for measuring solubilities. In this work the solubilities are determined using a chromatograph instead of the conventional gravimetric methods.

Ethane was withdrawn as a liquid from the solvent cylinder into the Ruska pump and was compressed to the desired pressure. Preliminary tests were conducted at varying flow rates from 500 cm^3/h to 40 cm^3/h. These tests were done for all the solutes at 308.15 K and at pressures of 50 bar and 200 bar. These tests demonstrated that at a flow rate of around 100 cm^3/h, the contacting time between the solvent and the solute is high enough to ensure equilibrium for all the systems at all conditions. In this work, all experiments were conducted at a solvent flow rate of 50 cm^3/h at pump conditions to ensure the achievement of equilibrium.

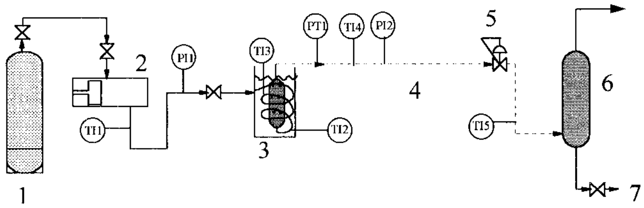

Figure 1. Schematic diagram of the experimental apparatus: (1) solvent cylinder; (2) Ruska pump; (3) extractor in constant temperature bath; (4) heat-traced line; (5) micrometering valve; (6) toluene bath; (7) sampling port; PI, pressure indicator; PT, pressure transducer; TI, thermocouple.

High-pressure ethane reached the desired temperature in a heat exchanger coil 10 m in length, immersed in a constant temperature bath (38 cm × 30 cm). The temperature in the bath was maintained using a temperature controller (Haake E-52). The temperature is monitored with a high-precision thermometer (±0.1 K) and thermocouples calibrated against the thermometer. The temperature bath was completely insulated with minimal heat loss to the surroundings. The accuracy of the temperature measurement is within ±0.1 K, and the temperature is maintained constant to within this accuracy. The extraction vessel (29 cm × 2.7 cm) is packed with a solid solute bed between 15 cm and 20 cm in height and is also immersed in the temperature bath. The extractor contained a mesh screen at the bottom and was also packed with glass beads between 3 cm and 5 cm in height. The supercritical solvent is passed through the extractor, and it exits the extractor saturated with the solute. Glass wool is packed at the top of the extractor (2 cm to 4 cm) to prevent entrainment of solid particles. The equilibrium pressure is measured with a pressure transducer (model 2088 Rosemount Measurement) accurate to ±0.4 bar. The mixture is then passed through a micrometering valve (Whitey SS22RS4) where it is expanded to atmospheric pressure. This valve was also used to control the pressure

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Table 1. Experimental Mole Fraction Solubilities (S) of n-Paraffins in Supercritical Ethane at 308.15 K

tetracosane		octacosane		dotriacontane	
P (bar)	10^3S	P (bar)	10^3S	P (bar)	10^3S
59.71	0.28 ± 0.004	55.84	0.54 ± 0.006	120.07	0.78 ± 0.007
74.83	3.67 ± 0.042	65.27	2.49 ± 0.033	136.73	0.89 ± 0.013
100.01	7.69 ± 0.13	78.13	3.01 ± 0.046	166.67	1.23 ± 0.015
129.99	11.11 ± 0.16	99.30	4.29 ± 0.062	200.68	1.53 ± 0.019
163.92	15.30 ± 0.34	140.32	8.51 ± 0.16		
199.32	20.55 ± 0.46	171.68	12.35 ± 0.27		
		200.64	15.87 ± 0.35		

in the extractor. The pressure of the extractor is maintained constant to within ±0.7% and the maximum deviation was ±0.15 bar at the highest pressure. The mixture is then passed through a bath (30 cm × 2.54 cm) filled with toluene where the solute from the solution is dissolved. To prevent the possible precipitation of the solid in the system, the entire line from the exit of the extractor to the toluene bath including the micrometering valve is heat traced and the temperature is maintained at around 423−473 K. The solvent gas leaving the toluene bath is subsequently passed through another toluene bath to ensure that all the solute is dissolved. No solute was found in the second toluene bath. Toluene was also flushed through the system at the end of each experimental run to dissolve any precipitated solid in the system. No solute was recovered from this flushed toluene for any of the experiments.

The amount of solute extracted is determined by a chromatographic analysis of the samples collected from the toluene bath. Liquid toluene samples with dissolved solute are injected into a Shimadzu GC-9A equipped with a capillary column with a chemically bonded stationary phase and dimensions 15 m × 530 μm and a film thickness of 1.5 μm (DB-5-15xw). The GC was calibrated against gravimetrically prepared samples of the solutes in toluene. The compounds were detected with a tungsten filament thermal conductivity detector (TCD). The amount of ethane pumped was obtained directly from the Ruska pump.

Source and Purity of Materials

The solutes tetracosane, octacosane, and dotriacontane used in this work were obtained from Aldrich Chemical Co. and were used without further purification. The stated purity of tetracosane and octacosane was over 99% and that of dotriacontane was over 97%. The solvent ethane, obtained from Linde Air Products, was of CP grade with over 99% purity.

Results and Discussion

The solubilities of tetracosane, octacosane, and dotriacontane in ethane at 308.15 K are presented in Table 1 along with the experimental uncertainties. The uncertainties in solubility (1% to 3%) arise mainly from the errors in the measurement of pressure and temperature which cause a 3% to 5% deviation in the density of ethane and the errors involved with the calibration of the GC (3%−4%). Repeatability tests were performed for the systems ethane + octacosane and ethane + tetracosane at both the low (50 bar) and high pressures (200 bar). The reproducibility of the solubility data over five to six experiments at each condition was within the experimental uncertainties reported here. The solubilities from Table 1 are plotted in Figures 2−4 for the systems octacosane, tetracosane, and dotriacontane, respectively. For comparison purposes, solubilities measured by Moradinia and Teja (1986) and Suleiman and Eckert (1995) are also shown. The fit of the data by the translated TBS EOS is also shown in these figures. The reliability of the apparatus was tested by measuring the solubilities of octacosane in supercritical ethane at a temperature of 308.15 K and pressures of 50 bar to 200 bar. The experimental values obtained in this work agreed with those of Moradinia and Teja (1986) and Suleiman and Eckert (1995) to within 0.2% and 5%, respectively, as shown in Figure 2. Figure 3 shows that the solubility obtained in this work for the system of ethane + tetracosane does not match with the results of Suleiman and Eckert (1995). Figure 4 shows that the solubility of dotriacontane from this work agrees well with that of Moradinia and Teja (1986) to within an average of 7%. The solubilities obtained by Suleiman and Eckert (1995) using the chromatographic method are considerably higher than those obtained in this work and in that of Moradinia and Teja (1986) for the system ethane + dotriacontane. A similar trend is observed for the system ethane + tetracosane.

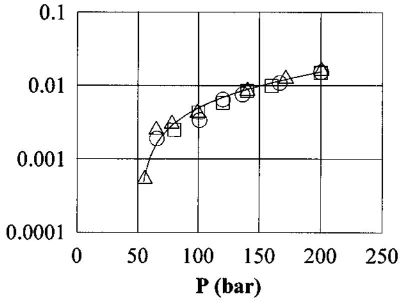

Figure 2. Mole fraction solubility S of octacosane in supercritical ethane at 308.15 K: (○) Moradinia and Teja (1986); (□) Suleiman and Eckert (1995); (△) this work. The solid lines were calculated using the translated TBS EOS.

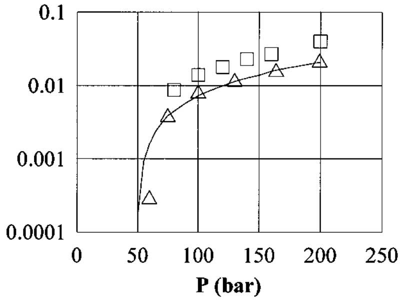

Figure 3. Mole fraction solubility S of tetracosane in supercritical ethane at 308.15 K: (□) Suleiman and Eckert (1995); (△) this work. The solid lines were calculated using the translated TBS EOS.

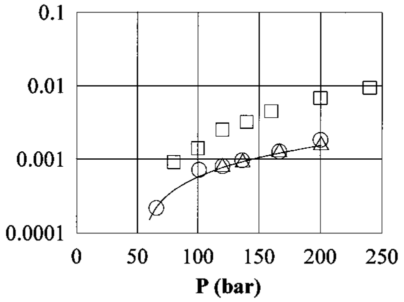

Figure 4. Mole fraction solubility S of dotriacontane in supercritical ethane at 308.15 K: (○) Moradinia and Teja (1986); (□) Suleiman and Eckert (1995); (△) This work. The solid lines were calculated using the translated TBS EOS.

The chromatographic method used by Suleiman and Eckert (1995) is an indirect method of measuring solubilities. The degree of retention of the solute in the supercritical fluid is only qualitatively related to the solvating power of the fluid. The validity of the method of deriving

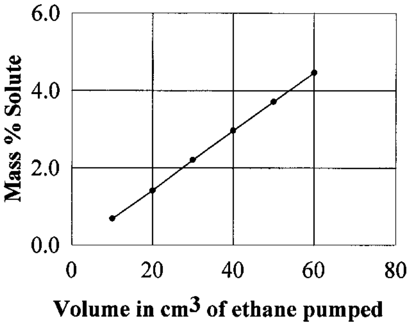

Figure 5. Dynamic sampling of toluene for ethane + octacosane.

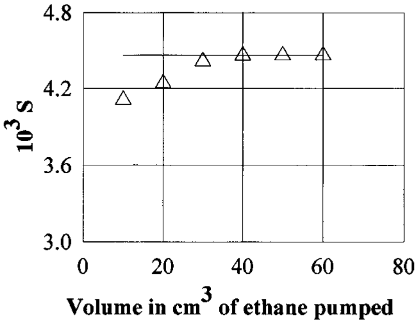

Figure 6. Experimental mole fraction solubilities S from dynamic sampling for ethane + octacosane.

the solubilities from capacity factors relies on several assumptions (Bartle et al., 1990) which are not always true. There is good agreement between the results obtained for the system ethane + dotriacontane in this work and by Moradinia and Teja (1986). Both these works used a flow type apparatus with the solute extracted from a packed column. Although a chromatographic technique is an attractive alternative to conventional methods of obtaining rapid phase equilibrium information, the results may not be accurate for all systems.

The method of dissolving the solute in toluene and subsequently using the chromatographic analysis of toluene to determine the amount of solute extracted gives this experimental design the additional capability of measuring solubilities as the experiment proceeds. This dynamic sampling procedure was used in this work to study the reliability of the solubility data. Figure 5 shows the results obtained from dynamic sampling for the system ethane + octacosane at 100 bar. The plot obtained for the mass % of octacosane in toluene against the amount of ethane pumped is linear, as expected, as the mixture leaving the extractor and entering the toluene bath is always saturated with the solute.

The advantage of dynamic sampling can be more clearly seen by translating the results obtained for mass % of solute in toluene from dynamic sampling into solubilities in ethane. The experimental solubility information obtained from the dynamic sampling data of Figure 5 is shown here in Figure 6. The initial two data points underpredict the solubility by about 10% compared to the solubility value reported in this work. Thus, the method of dynamic sampling quantifies the entrance effects and offers more insight into the dynamics of the experimental apparatus.

Data Correlation

The solubilities obtained in this work were correlated using the principle of translation of a cubic EOS at the triple point to represent solid phases in equilibrium. The principle and methodology involved in the translation of EOS as applied to the Trebble–Bishnoi–Salim (TBS) equation can be found elsewhere (Salim and Trebble, 1994). The solid lines depicted in Figures 2–4 show the performance of the model in representing the solid solubilities. Two interaction parameters k_a and k_d were used along with the conventional mixing rules to represent the experimental data. Table 2 shows the results of the regression of the solubility data.

Table 2. Regression of Equilibrium Solubility Data with Translated TBS EOS

system	k_a	k_d	% AAD	% SD of k_a	% SD of k_d
tetracosane + ethane	−0.0147	−0.3128	4.25	1.76	6.53
octacosane + ethane	−0.2009	−0.6544	10.65	1.97	5.66
dotriacontane + ethane	−0.1185	−0.9131	2.00	2.42	4.48

Table 2 shows that the translated TBS EOS represents the solubility data quite well. There is no definite trend in the interaction parameters but as the carbon number of the solute increases, the correction introduced by the interaction parameters to the geometric mean rule also increases.

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