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Solubility of Dichlorobis(triphenylphosphine)nickel(II) in Supercritical Carbon Dioxide

Daniel R. Palo and Can Erkey*

Environmental Engineering Program, Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06269

The solubility of dichlorobis(triphenylphosphine)nickel(II) in supercritical carbon dioxide was determined using a dynamic method. Solubility isotherms were obtained at (308, 318, and 328) K in the pressure range (10.8 to 27.9) MPa. Solubilities increased linearly with increasing density at constant temperature and increased with increasing temperature at constant density.

Introduction

The discovery of the ability of transition metal complexes to catalyze reactions in supercritical carbon dioxide (SC-CO_2) has opened up new horizons in the development of highly selective, environmentally friendly manufacturing processes for a wide variety of chemicals (Rathke et al., 1991; Jessop et al., 1995, 1996; Morgenstern et al., 1996). Advantages of using $SCCO_2$ as a solvent may include increased reaction rates, higher selectivities, and facile separation of reactants, catalysts, and products after reaction. Moreover, $SCCO_2$ is nontoxic, nonflammable, environmentally acceptable, inexpensive, and readily available in large quantities and has a low critical temperature and a moderate critical pressure.

The most successful and widely used transition metal catalysts contain triphenylphosphine (PPh_3). A knowledge of the solubility of such complexes in $SCCO_2$ is important for further theoretical and practical developments in utilizing $SCCO_2$ as a solvent in homogeneous catalysis. Such data do not exist, and therefore, we have measured the solubility of one such compound, dichlorobis(triphenylphosphine)nickel(II), in $SCCO_2$. Dichlorobis(triphenylphosphine)nickel(II) has been employed as a selective hydrogenation, isomerization, and hydroboration catalyst (Iyer and Varghese, 1995; Itatani and Bailar, 1967; Baruah and Sen, 1994).

Experimental Section

A schematic diagram of the experimental apparatus for solubility measurements is given in Figure 1. For a typical run, a supercritical fluid extraction vessel (7-Valco, SFED.625-5) with an internal volume of 10 cm^3 is packed with powdered dichlorobis(triphenylphosphine)nickel(II) and placed in a constant temperature (±0.5 K) oven (6-Thelco, 2DG). Liquid carbon dioxide from a cylinder equipped with a dip tube (1) is cooled in a refrigeration unit (2-Boekel, 260013) and compressed into syringe pumps (4, 5-ISCO 260D) using a high-pressure liquid pump (3-TSP, miniPump). The syringe pump (4) is started, and liquid carbon dioxide is delivered at a constant flow rate through a four-way switching valve (8-Valco, 4UW). This stream is mixed with the ethanol stream delivered by a high-pressure liquid pump (3-TSP, miniPump), and the mixture is expanded through a back-pressure regulator (10-Tescom, 26-1722-24-194). A liquid−gas separator (13), placed after the back-pressure regulator, is used to vent off the CO_2 and collect the ethanol. After a steady flow rate is established, the second syringe pump (5) is started and the valve (8) is switched. The CO_2 stream from the syringe pump (5) is passed through the extraction vessel and gets saturated with dichlorobis(triphenylphosphine)-nickel(II). This stream is diluted with the pure CO_2 stream from the syringe pump (4) in the oven to prevent precipitation due to retrograde condensation. The diluted mixture is then passed through the switching valve, mixed with the ethanol stream, and passed through the back-pressure regulator. The two-phase mixture is then sent to a collection vial (12) where gaseous CO_2 is vented off. The dichlorobis(triphenylphosphine)nickel(II)/ethanol solution is collected for a certain period of time and analyzed off-line using an ultraviolet spectrophotometer (Milton Roy, Spectronic 601) operating at 252 nm. On the basis of sample collection time, the mass of ethanol solution, concentration of the dichlorobis(triphenylphosphine)nickel-(II) in ethanol, and CO_2 flow rate through the extraction vessel, the solubility of dichlorobis(triphenylphosphine)-nickel(II) in $SCCO_2$ is readily calculated.

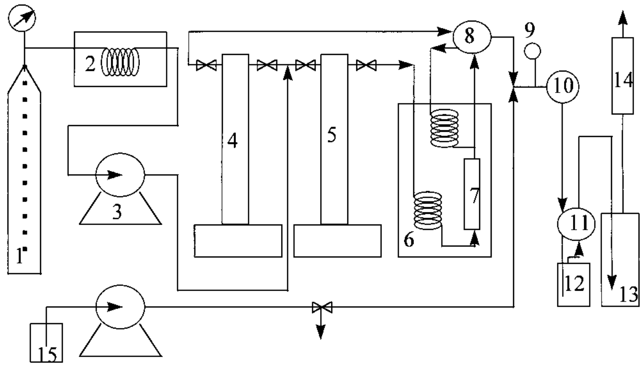

Figure 1. Schematic diagram of the apparatus: 1, carbon dioxide cylinder; 2, refrigeration unit; 3, liquid pump; 4, syringe pump; 5, syringe pump; 6, oven; 7, extraction vessel; 8, switching valve; 9, pressure transducer; 10, back-pressure regulator; 11, switching valve; 12, sample collection; 13, gas−liquid separator; 14, carbon trap; 15, solvent reservoir.

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* To whom inquiries should be addressed. E-mail: cerkey@eng2.uconn.edu.

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Table 1. Mole Fraction Solubility S of Phenanthrene in Supercritical Carbon Dioxide at 318 K and 16.3 MPa

Kurnik et al. (1981)		Cross et al. (1996)		this work	
10^3S	$10^3\sigma$	10^3S	$10^3\sigma$	10^3S	$10^3\sigma$
1.40	n/a	1.38	0.12	1.52	0.25

Table 2. Mole Fraction Solubility S of Dichlorobis(triphenylphosphine)Nickel(II) in Supercritical Carbon Dioxide of Density ρ

P/MPa	ρ/kg·m^{-3}	10^6S	$\sigma/10^6S$
	$T = 308$ K		
10.8	739.	1.32	0.15
14.0	802.	1.75	0.18
19.4	861.	2.10	0.18
22.2	883.	2.19	0.20
24.9	901.	2.11	0.16
27.7	918.	2.41	0.05
	$T = 318$ K		
13.7	715.	1.68	0.23
16.5	769.	2.47	0.33
18.2	795.	3.02	0.29
22.2	835.	3.64	0.13
24.9	857.	3.73	0.10
27.9	878.	4.41	0.07
	$T = 328$ K		
13.8	612.	1.69	0.18
16.7	698.	3.13	0.51
19.5	749.	3.93	0.11
21.9	779.	4.42	0.14
24.9	810.	4.82	0.17
27.6	833.	5.33	0.20

Typical flow rates through the extraction vessel are around 20 g/h of CO_2 to ensure saturation. A pressure transducer (9-Omegadyne, PX01K1-5KGV) with an accuracy of ±35 kPa is employed to monitor the operating pressure of the system. The operating temperature is monitored by a thermocouple meter (DP41-TC-MDSS, Omega Engineering) connected to a T-Type thermocouple (Omega Engineering) inside the oven. Temperature measurements are accurate to ±1 K. Dichlorobis(triphenylphosphine)nickel(II), with a purity of 98%, was purchased from Sigma Chemicals and was used as received. Carbon dioxide was purchased from Connecticut Airgas and had a stated purity of 99%.

The accuracy of the instrument was checked against binary solubility data in the literature for phenanthrene/$SCCO_2$ at 308 K and 16.3 MPa. A comparison of the data obtained using our instrument and the data in the literature is given Table 1. The three data points agree within experimental error.

Results

The data are presented in Table 2 along with the CO_2 density, which was calculated using an equation of state given by IUPAC (Angus et al., 1971). Each data point is the average of six consecutive samples. The relative standard deviations (RSD) ranged from (1.4 to 16)%, with an average RSD of 7.4%. The solubility increases with increasing density at constant temperature and with increasing temperature at constant density. Figure 2 shows a linear relationship between solubility and density at constant temperature. The coefficients of the equations that represent each regression line are given in Table 3.

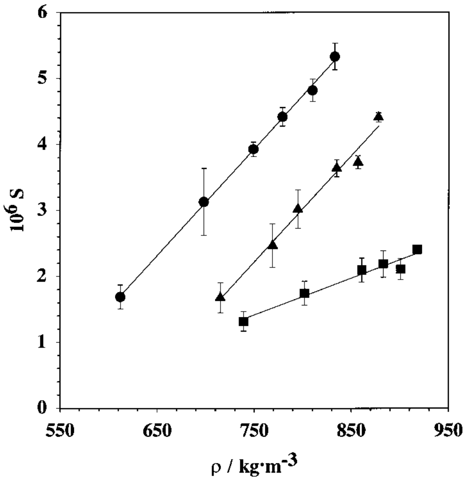

Figure 2. Variation of mole fraction solubility S with temperature and CO_2 density ρ: ■, 308 K; ▲, 318 K; ●, 328 K.

Table 3. Coefficients for the Fit $S = a\rho + b$, S[=]mol/mol, ρ[=]kg·m^{-3}

T/K	10^8a/m^3·kg^{-1}	10^6b
308	0.557	−2.76
318	1.60	−9.81
328	1.62	−8.18

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