Solubilities of 5, 10, 15, 20-Tetrakis (pentafluorophenyl) -21*H*, 23*H*-porphine iron(III)chloride in Supercritical Carbon Dioxide

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A flow system for the determination of the solubilities of naphthalene and Fe-porphine catalyst in supercritical carbon dioxide (SCCO$_2$) is investigated at different temperatures and pressures. The results for the solubility of naphthalene in SCCO$_2$ agreed very well with the data from the literature, in spite of the different operating conditions. The solubility of the catalyst increased as the pressure was increased at a constant temperature. Meanwhile their solubility decreased as the temperature was increased at a constant pressure. The solvent density was the main parameter that controlled the solubility of the catalyst in the solvent.

Key words: solubility, catalyst, supercritical carbon dioxide.

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ค่าการละลายของตัวเร่งปฏิกิริยา 5, 10, 15, 20- เตตระคิส(เพนตะฟลูออโรฟีนิล)-21*H*, 23*H*-พอร์ฟีน เหล็ก(III) คลอไรด์ในคาร์บอนไดออกไซด์ภาวะเหนือวิกฤติ

สมเกียรติ งามประเสริฐสิทธิ์, เซียวเวิ่น วู และ เซอิชิโร โคดะ (2542)
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งานวิจัยนี้เป็นการหาค่าการละลายของแนฟทาลีน และตัวเร่งปฏิกิริยาเหล็ก-พอร์ฟีน ในคาร์บอนไดออกไซด์ภาวะเหนือวิกฤติ ในระบบที่มีการไหลต่อเนื่องที่อุณหภูมิและความดันต่างๆกัน ผลของการทดลองหาค่าการละลายของแนฟทาลีนสอดคล้องอย่างดีกับข้อมูลการทดลองของผู้วิจัยอื่นแม้ว่าภาวะการทดลองจะแตกต่างกัน ส่วนค่าการละลายของตัวเร่งปฏิกิริยา พบว่ามีค่าเพิ่มขึ้นตามความดันที่เพิ่มขึ้น ณ อุณหภูมิคงที่ค่าหนึ่ง ในขณะที่ค่าการละลายลดลงเมื่ออุณหภูมิสูงขึ้นที่ความดันคงที่ค่าหนึ่ง จากผลการทดลองดังกล่าวสามารถสรุปได้ว่าพารามิเตอร์สำคัญที่ควบคุมการละลายของตัวเร่งปฏิกิริยาในตัวทำละลายนี้ก็คือความหนาแน่นของตัวทำละลายนั่นเอง

คำสำคัญ ค่าการละลาย, ตัวเร่งปฏิกิริยา, คาร์บอนไดออกไซด์ภาวะเหนือวิกฤต

INTRODUCTION

A fluid is said to be "supercritical" when its temperature and pressure exceed the temperature and pressure at the critical point.

Figure 1 shows an example of the vapor pressure curve and the critical point at which the curve terminates. Table 1 lists the critical temperature and pressure for various fluids. CO_2 and water are the fluids which are most frequently used in reactions at supereritical conditions. Co_2 has often been because it has a critical temperature near ambient conditions. Water, which possesses a much higher critical temperature and pressure, has been used frequently in reaction studies because of potential applications of reactive processes at supercritical conditions that employ water.

Figure 1. Vapor pressure curve and critical point of a fluid.

Table 1. Critical Temperature and Pressure of Selected Fluids.

Fluid	T_c (K)	P_c (atm)
Ethylene	282.4	49.7
Carbon dioxide	304.2	72.8
Ethane	305.4	48.2
Nitrous oxide	309.6	71.5
Propane	369.8	41.9
Ammonia	405.6	111.3
Methyl amine	430.0	73.6
t-Butanol	506.2	39.2
n-Hexane	507.4	29.3
Acetone	508.1	46.4
Methanol	512.6	79.9
Ethanol	516.2	63.0
Toluene	591.7	40.6
p-Xylene	616.2	34.7
Water	647.3	217.6

Supercritical fluids (SCFs) exhibit many unique properties and are used in various chemical reactions as solvents. Many of the physical and transport properties of an SCF are intermediate between those of a gas and a liquid. Table 2 represents order of magnitude values for some SCF properties relevant to chemical reactions.(1) The diffusivity in an SCF is between that in a gas and a liquid, therefore the reactions that are diffusion-controlled in the liquid phase could become faster in an SCF phase.

Table 2. Comparison of Typical SCF, Gas, and Liquid Properties.

	Gas	SCF	Liquid
Density (g/cm^3)	10^{-3}	0.1-0.5	1
Viscosity(Pa.s)	10^{-5}	10^{-4}-10^{-5}	10^{-3}
Diffusivity (cm^2/s)	10^{-1}	10^{-3}	10^{-5}

Figure 2. Experimental solubilities for solid naphthalene and solid biphenyl in supercritical carbon dioxide at various temperatures.[2]

SCFs also have unique solubility properties. Compounds that are largely insoluble in a fluid at ambient conditions can become soluble in a fluid under supercritical conditions. Conversely, some compounds that are soluble at ambient conditions can become less soluble at under supercritical conditions. Figure 2 shows experimental data for naphthalene solubility in $SCCO_2$ and salt solubility in water(1) that illustrate this effect.

In recent years, the applications of SCFs have widely expanded, especially in chemical reactions. They include Diels-Alder reactions, organometallic reactions, heterogeneously catalyzed reactions, fuel processing, oxidation chemistry, electrochemistry, biomass utilization, polymerization, and materials synthesis.(1)

The aerobic oxidation of cyclohexane catalyzed by Fe(III)(5,10,15,20-tetrakis (pentafluorophenyl)porphine)Cl in sub- and super-critical CO_2 has been studied.(3) The reaction rate had a maximum value in the neighborhood of the critical pressure. We therefore investigate the solubility of Fe(III)(TPFPP)Cl [TPFPP = 5,10,15,20-tetrakis (pentafluorophenyl) porphine] in supercritical CO_2 in order to finding the influence of the pressure and temperature by using a spectrometric method.(4) This method is used following a flow system and precipitation by dissolving the solute in a suitable solvent and making photometric measurements on the solution after calibration with standard solutions. In addition, we aim to use the dissolved catalyst at saturation and for a single phase for the other oxidation reactions in the SC fluid.

EXPERIMENTAL SECTION

A schematic diagram of the experimental apparatus is shown in Figure 3. Liquid carbon dioxide from a cylinder is passed a cooler at a constant temperature of –9ºC, charged into a high-pressure liquid pump (Jasco, model PU-980 intelligent HPLC pump) and compressed to the desired pressure. The flow rates from this pump are maintained in the range of 0.1 ml/min to 0.4 ml/min. After reaching a constant temperature with a heating coil around the lines, carbon dioxide enters the equilibrium cells connected in series. A 0.5-micron filter element with an inside diameter of 4.5 mm and inside height of 11.2 mm is packed with catalyst and put inside each equilibrium cell. The number of cells is 2 or 3 depending on the experiment. After exiting the last cell, the saturated solution flows through a check valve, a pressure transducer and a back pressure regulator. The pressure is maintained constant to within ±1 kg/cm^2 of the desired value throughout an experiment. After reaching the desired pressure, a suitable solvent (flushed solvent) is fed after the check valve by a high-pressure pump (Jasco, model PU-980 intelligent HPLC pump). The flow rate of flushed solvent is selected to be suitable for the direct measurement of concentration without further preparation. The outlet of the mixture from the back pressure regulator is expanded and connected to a gas-liquid separator (in an ice bath). The concentration of solute in liquid solution is then determined using UV-spectrometric techniques. The flow rate of the gaseous carbon dioxide is subsequently determined by means of a water displacment technique. The liquid solution is collected to determine the average concentration every ten minutes for one hour.

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

Initial experiments were performed with naphthalene and CO_2 to demonstrate that the solubility determination system operated at equilibrium. The experiments were carried out to compare the results with published data(2) and to establish appropriate experimental procedures. Naphthalene-CO_2 experiments were conducted at constant temperatures of 35, 55, and 60°C, and at various pressures between 81.3 and 200.3 atm. Two or three equilibrium cells, naphthalene mixed with 1-mm diameter glass beads, and different flow rates of CO_2 were operating conditions for assuring the saturated values. The size of the filter element for naphthalene was larger than that for the catalyst (9.2 mm inside diameter and 14.1 mm inside height) because its solubility in $SCCO_2$ is very large.

RESULTS AND DISCUSSION

The experimental solubility data for solid naphthalene in supercritical carbon dioxide at 35, 55, and 60°C are presented in Table 3. Our results agree very well with the data of McHugh(2) at every temperature over the entire pressure range, even though the flow rate was doubled and the number of reactors changed from 2 reactors to 2 reactors with glass beads and 3 reactors. We therefore assured that our system of solubility determination is well established.

Solubility of Catalyst with CO_2

Experiments were performed at a series of pressures and temperatures. The effect of the solvent density on solubility was studied at different pressures at constant temperatures of 30, 35, 50, 60, and 70°C. The results are shown in Table 4. The solubility increased as the pressure was increased. Pure CO_2 densities are also listed in Table 4. The CO_2 densities in Table 4 were obtained by HYSYS version 1.2.7 simulation software using Peng Robinson property package. The increase in solubility as a function of pressure was related to a corresponding increase in CO_2 density.

Table 3. Experimental Solubilities for Naphthalene in Supercritical Carbon Dioxide.

Pressure	Mole fraction			
atm	2 reactors	2 reactors with glass beads	3 reactors	McHugh[2]
	T = 35°C			
81.3	0.0077			0.00750 (85.7 atm)
102.6	0.0101 (0.0101)	0.0114		0.01066 (105.1 atm)
125.8	0.0147	0.0143		0.01410 (131.3 atm)
165.5	0.0155			0.01605 (166.8 atm)
200.3	0.0163			0.01709 (196.9 atm)
	T = 55°C			
82.3	0.0016			0.00131 (81.1 atm)
104.5	(0.0065)	0.0065		0.00546 (108.3 atm)
126.8		0.0200	0.0197	0.02114 (131.5 atm)
158.7			0.0327	0.03053 (158.5 atm)
	T = 60°C			
106.5	(0.0050)	(0.0050)		0.00524 (107.0 atm)
129.7		0.0176		0.01516 (132.1 atm)
162.6			0.0413	0.03401 (162.1 atm)

Flow rate of carbon dioxide (liquid from feed pump) = 0.2 ml/min,
in parentheses = 0.4 ml/min.

Figure 4. Solubilities of Catalyst with CO_2 as a Function of Temperature.

Table 4. Experimental Solubilities for 5,10,15,20-Tetrakis(pentafluorophenyl)-21H,23H-porphine iron(III) chloride in Supercritical Carbon Dioxide at Various Temperatures and Pressures.

Pressure atm	Mole Fraction μgmol/gmol	Density of CO_2 g/cm^3
T = 30°C		
77.4	0.4037	0.6336
101.6	1.0290	0.6951
128.7	1.9137	0.7341
157.8	3.0044	0.7630
196.5	4.9944	0.7915
T = 35°C		
101.6	0.9465	0.6638
128.7	1.4379	0.7488
157.8	2.6035	0.8055
195.5	4.4658	0.8583
T = 50°C		
128.7	0.3486	0.5840
157.8	1.3657	0.6805
194.5	3.2169	0.7562
T = 60°C		
157.8	0.6349	0.5920
196.5	2.2655	0.6896
T = 70°C		
157.8	0.2402	0.5098
194.5	1.5072	0.6164

Flow rate of carbon dioxide (liquid from feed pump) = 0.3 ml/min.

The solubility as a function of temperature and at a constant pressure of 157.8 atm are presented in Figure 4. The solubility decreased as the temperature was increased. It was also related to a corresponding decrease in CO_2 density.

Solubility of the Catalyst at Various Flow Rates of CO_2

The solubility of the catalyst was measured at different flow rates of CO_2. The results are shown in Table 5 and Figure 5. The solubility is approximately constant and independent of the overall flow rates. We therefore assure that the system is well developed for the determination of the solubility of some solids in supercritical CO_2 and the system can be applied for homogeneous contact of the catalyst with other fluids.

Table 5. Experimental Solubility of the Catalyst in Supercritical Carbon Dioxide at Different Flow Rates (liquid from Feed Pump).

Flow Rate ml/min	Mole Fraction μgmol/gmol
0.1	2.8490
0.2	2.7292
0.3	2.6035
0.4	2.7140

Figure 5. Experimental Solubility of the Catalyst in $SCCO_2$ at Different Flow Rates.

CONCLUSIONS

1. The flow system of solubility determination for the catalyst in $SCCO_2$ is well developed.
2. The solvent density was the main parameter that controlled the solubility of the catalyst in the solvent.

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