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Solubilities of Phenol and Pyrocatechol in Supercritical Carbon Dioxide

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The solubilities of phenol and pyrocatechol (1,2-dihydroxybenzene) in supercritical carbon dioxide were measured over the temperature range from 333.15 K to 363.15 K and the pressure range from 100 bar to 350 bar. The data were obtained using a recirculating equilibrium apparatus, which was tested by measuring the solubility of naphthalene in supercritical carbon dioxide. The measured solubilities were correlated using a semiempirical model proposed by Bartle.

Introduction

Supercritical fluid (SCF) solvents are now in widespread use for a large variety of applications. Supercritical carbon dioxide ($scCO_2$) especially is of interest because of its selective, cheap, and environmental friendly replacement of traditional organic solvents. Nowadays, supercritical fluid extraction (SFE) using $scCO_2$ is a well-established process that has been used commercially for more than two decades in the food industry.[1] In contrast, one very interesting and, as yet, not fully investigated area of SCF technology is the use of a supercritical solvent as a reaction medium in which the solvent either actively participates in the reaction or functions solely as the solvent medium for the reactants, catalysts, and products.[2] A common element of any application of SCF technology being considered in current research is the requirement of a thorough understanding and knowledge of the solubility of the compounds of interest in SCF. Once the solubilities of the compounds are known, a first approach to the technical and economic feasibility of any SCF process can be established.

In this paper the solubilities of phenol and pyrocatechol (1,2-dihydroxybenzene) have been measured in supercritical carbon dioxide over the temperature range from 333.15 K to 363.15 K and the pressure range from 100 bar to 350 bar to assist in the study of the selective oxidation of phenol. Although some results have been reported for the solubility of phenol at 309.15 K and 333.15 K[3] at 308.15 K, 318.15 K, 328.15 K, and 338.15 K,[4] no solubility data of these compounds have been published throughout the reaction temperature range of interest.

Experimental Section

Materials. Carbon dioxide supplied by Praxair had a minimum purity of 99.996%. Phenol and pyrocatechol with a minimum purity of 99.5% were obtained from Fluka. Acetone (HPLC grade) was obtained from Scharlab. Glass beads (3 mm) were obtained from Afora. All chemicals were used directly without further purification.

Apparatus. Figure 1 shows a schematic diagram of the apparatus assembled in our laboratory to perform solubility measurements with a recirculating equilibrium method. Liquid carbon dioxide from a cylinder with a siphon attachment is first passed through a check valve (Autoclave Engineers, UKO2200) and a 2 μm filter (Valco, ZUFR2F) in order to prevent reverse flow and remove the possible particles from the cylinder, respectively. Then it is compressed to the operating pressure by a dual plunger type high-pressure pump (Jasco, PU-986) equipped with a cooling jacket. An ethylene glycol stream at −15 °C from a refrigerating bath (Julabo, F30) is used to ensure liquid carbon dioxide in the pump head. The stream from the pump is sent to a closed-loop by opening the two-way valve 12 (Autoclave Engineers, 10V2071) and closing the two-way valve 11 (Autoclave Engineers, 10V2072). A gears type recirculating pump (Micropump, 1805C) is used to circulate the fluid through a 50 mL (1 in. i.d. × 9 cm) supercritical fluid extraction vessel (Valco, SFE1-E), a six-ports/two-positions valve (Valco, 2C6UWEY) with a 100 μL sample loop attached, and a 100 mL (1.2 in. i.d. × 6.3 in.) high-pressure view cell (Thar Designs, Inc.) with two sapphire windows mounted in an axial orientation. Two on/off valves (Valco, SFVO) and a prime/purge valve (Valco, SFV) also are connected to the six-ports/two-positions valve for sampling purposes. Temperature and pressure are monitored continuously in the CO_2 recirculating stream by means of a K type thermocouple and a pressure transducer (Trafag, 8891.84.3315). The uncertainties of the temperature and pressure measurements were ±1 K and ±1 bar, respectively. A safety head (Autoclave Engineers, SS2600) equipped with a rupture disk rated to a burst pressure of 425 bar at 293 K, two two-way valves (Autoclave Engineers, 10V2071) and a three-way valve (Autoclave Engineers, 10V2073) are installed into the closed-loop for safety and cleaning reasons, respectively. To release slowly the supercritical solution from the system at the end of an experiment, a micrometering valve 10 (Autoclave Engineers, 10VRMM) is installed in the outlet line. All the devices in this closed-loop are immersed in a water bath for temperature control equipped with an immersion circulator (JULABO, MD), having an accuracy of ±0.1 K. Before the gas solution is released to the vent, it is directed through two cold traps, where the solid solutes are separated, and a CO_2 mass flow meter (Bronkhorst High-Tech, F-111C-HD-22-V) with a measurement range of 0.2−10 N dm^3/min and an uncertainty within ±1% of the full-scale range. Data acquisition software, Adkir (ICP-CSIC), was

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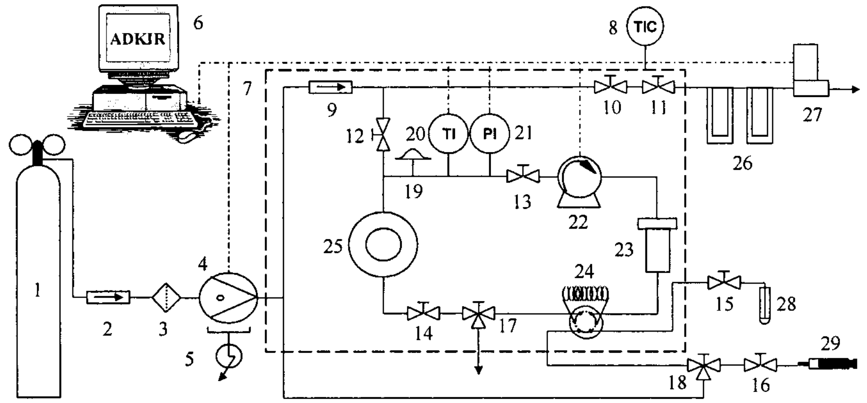

Figure 1. Schematic diagram of recirculating equilibrium apparatus for solubility measurements: (1) CO_2 tank; (2, 9) check valves; (3) filter; (4) high-pressure pump; (5) refrigerating bath; (6) data acquisition software; (7) thermostatized bath; (8) temperature controller; (10) micrometering valve; (11−16) two-way valves; (17−18) three-way valves; (19) rupture disk; (20) temperature indicator; (21) pressure indicator; (22) recirculating pump; (23) SFE vessel; (24) six-ports/two-positions valve with 100 μL loop attached; (25) view cell; (26) cold traps; (27) mass flow meter; (28) collection vial; (29) syringe.

used to register the electronic signal from the measurement devices (viz., thermocouple, pressure transducer, and mass flow meter) as well as to start/stop both pumps.

Experimental Procedure. In a typical experiment, solid solutes were packed into the SFE vessel between layers of glass beads. Air was initially removed from the system by passing CO_2 gas through it. The system was then thermostatized to the desired temperature. The high-pressure pump was next activated until pressurization of the system was accomplished. After a set pressure was reached, equilibrium solubility was attained by recirculating the supercritical fluid through the closed-loop for 30 min. This time was determined by experiments up to 2 h to be more than sufficient to reach equilibrium. The recirculating pump was operated at 500 rpm, which means a recirculating flow of roughly 20 mL/min. After the equilibration time, the six-ports/two-positions valve was rotated to allow 100 μL of the supercritical solution to be expanded between valves 15 and 16. Then valve 15 was opened slowly and the effluent was depressurized and bubbled into a collection vial containing acetone for off-line analysis. Finally, valves 15 and 16 were opened completely and by means of a syringe fitted in valve 16 the solvent from the collection vial was sucked up and injected again several times through the sample loop to recover the precipitated solid. Before the six-ports/two-positions valve was rotated back to the load position, the sample loop was cleaned with fresh solvent and filled up with pressurized carbon dioxide by means of valve 18. Then the system pressure was raised to obtain other solubility data. When a solubility isotherm was finally obtained, the apparatus was depressurized and cleaned thoroughly first with acetone and next with pressurized carbon dioxide, the SFE vessel was filled up again with solid solute and glass beads, and the procedure described above was repeated to obtain another solubility isotherm.

The samples collected in acetone were analyzed with a Varian 3800 gas chromatograph equipped with a flame ionization detector, a 30 m × 0.250 mm (film thickness = 0.25) CP-Sil 8CB wall-coated open tubular column (Chrompack), and Varian Star Chromatography software, which enables instrument control and data handling on a Microsoft Windows-based platform.

Results and Discussion

The reliability and efficiency of the solubility measurement technique were previously established by measuring the solubility of naphthalene in CO_2 at 308.15 K and different pressures. A comparison of the data from this work and those of two other researchers is showed in Table 1.[5,6] In this work, each data point represents the average of six measurements determined with a precision within ±3%. The agreement with existing data is excellent. These results confirm that the developed technique guaranteed adequate precision and accuracy.

Table 1. Solubilities of Naphthalene in Supercritical Carbon Dioxide at 308.15 K

	10^2y		
P/MPa	Iwai et al., 1991	Fat'hi et al., 1998	this work
13.8	1.41	1.52	1.52
16.8	1.65	1.62	1.65
20.4	1.76	1.74	1.73

Table 2. Solubilities of Phenol in Supercritical Carbon Dioxide

	T = 333.15 K		T = 348.15 K		T = 363.15 K	
P/MPa	ρ/kg·m^{-3}	10^3y	ρ/kg·m^{-3}	10^3y	ρ/kg·m^{-3}	10^3y
10.0	291	1.14	234	1.84	203	2.04
12.5	475	5.34	343	3.46	282	3.25
15.0	607	13.60	466	7.35	373	7.49
17.5	679	23.60	562	16.31	461	11.53
20.0	725	36.00	628	27.92	535	19.79
22.5	760	40.65	676	36.27	592	27.99
25.0	788	44.62	713	40.20	637	38.66
27.5	811	54.38	743	55.65	674	51.71
30.0	831	59.90	768	62.10	704	65.39
32.5	848	67.82	789	70.50	730	77.49
35.0	864	77.30	809	80.91	753	90.64

The solubilities of phenol and pyrocatechol in supercritical carbon dioxide were determined at 333.15 K, 348.15 K, and 363.15 K from 100 bar to 350 bar. The experimental results are listed in Tables 2 and 3 in terms of the mole fraction of solute. Pure CO_2 density values as a function of the pressure are also reported, being calculated by an equation of state formulated by IUPAC.[7] All of the experimental data points represent solid−fluid equilibrium, without a liquid phase present, as verified by looking into the view cell. The reported values are the average of three measurements with a percentage relative standard deviation of ±5%.

For both solutes it was observed that the solubility increases with temperature and with density, the increase with density being more pronounced at high temperatures. The solubility of phenol and pyrocatechol increased by a

Table 3. Solubilities of Pyrocatechol in Supercritical Carbon Dioxide

	$T = 333.15$ K		$T = 348.15$ K		$T = 363.15$ K	
P/MPa	ρ/kg·m^{-3}	10^4y	ρ/kg·m^{-3}	10^4y	ρ/kg·m^{-3}	10^4y
10.0	291	1.22	234	1.48	203	2.10
12.5	475	3.35	343	3.45	282	2.83
15.0	607	10.78	466	5.69	373	4.53
17.5	679	16.25	562	10.31	461	9.06
20.0	725	19.90	628	15.24	535	14.63
22.5	760	22.73	676	19.17	592	19.63
25.0	788	26.08	713	23.58	637	24.00
27.5	811	27.38	743	27.08	674	29.00
30.0	831	29.57	768	30.96	704	36.56
32.5	848	29.98	789	34.94	730	40.65
35.0	864	30.54	809	38.47	753	45.83

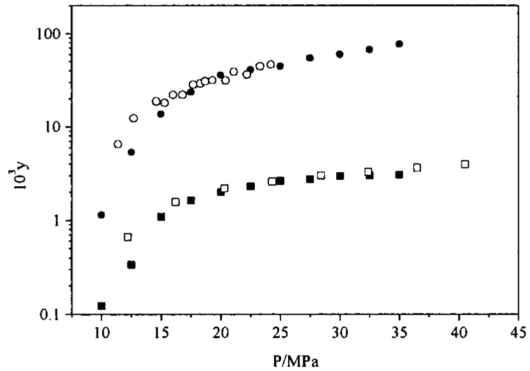

Figure 2. Solubility isotherms of phenol and pyrocatechol in supercritical CO$_2$: (●) phenol solubilities in this work at 333.15 K; (○) phenol solubilities at 333.15 K from ref 3; (■) pyrocatechol solubilities at 333.15 K in this work; (□) pyrocatechol solubilities at 338.15 K from ref 4.

factor of 80 and 38, respectively, from the temperature 333.15 K and the pressure 100 bar to the temperature 363.15 K and the pressure 350 bar. Phenol showed solubility approximately 20-fold higher than pyrocatechol at the higher pressure. A comparison of these results with the solubility measurements available in the literature for phenol at 333.15 K and pyrocatechol at 338.5 K is shown in Figure 2. As can be seen from the graph, there is fairly good agreement in the solubility data between this work and the literature.

The measurement solubilities were correlated using a semiempirical model proposed first by Bartle[8] and used afterward successfully by others.[9–12] The correlation equation is given in eq 1

$$\ln(yp/p_{\mathrm{ref}}) = A + c(\rho - \rho_{\mathrm{ref}}) \qquad (1)$$

where y is the mole fraction solubility, p is the pressure, A and c are constants, p_{ref} is a standard pressure of 1 bar, ρ is the density of the solution, and ρ_{ref} is a reference density, for which a value of 700 kg m^{-3} was used for calculations. The reason for using ρ_{ref} is to make the value of A much less sensitive to experimental error in the data and to avoid the large variations caused by extrapolation to zero density. A is given by

$$A = a + b/T \qquad (2)$$

where T is the absolute temperature. Combining eqs 1 and 2, the correlation equation becomes

$$\ln(yp/p_{\mathrm{ref}}) = a + b/T + c(\rho - \rho_{\mathrm{ref}}) \qquad (3)$$

Table 4. Parameters Used in the Calculation of Solubilities from Eq 3

	a	b/K	10^3c/m^3 kg^{-1}	AARD[a]
phenol	16.7	−5005	9.10	5.9
pyrocatechol	13.3	−4837	7.88	5.9

[a] AARD $= (1/N)[\sum_{i=1}^{N} |\{y_i - y_i^{\mathrm{cal}}\}/y_i|] \times 100$, where the superscript "cal" denotes calculated mole fraction solubility.

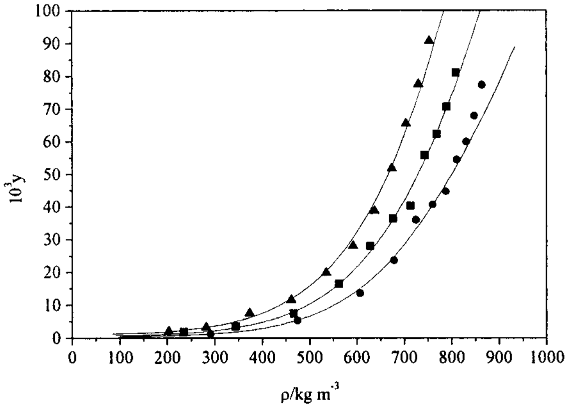

Figure 3. Solubility in mole fraction, y, for phenol in supercritical CO$_2$. The graph shows the comparison of predicted curves (lines) and experimental points of the solubility plotted versus density, ρ: (●) 333.15 K; (■) 348.15 K; (▲) 363.15 K.

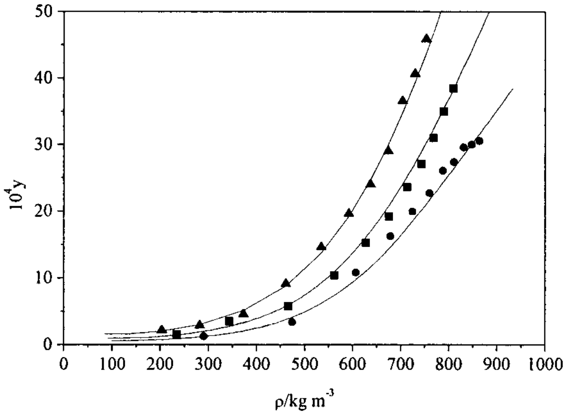

Figure 4. Solubility in mole fraction, y, for pyrocatechol in supercritical CO$_2$. The graph shows the comparison of predicted curves (lines) and experimental points of the solubility plotted versus density, ρ: (●) 333.15 K; (■) 348.15 K; (▲) 363.15 K.

From the experimental data, each isotherm was fitted using eq 1 to obtain the values of A and c. The values of c were then averaged for each compound, and the values given in Table 4 were obtained. Afterward, the values of A were plotted against $1/T$ for each compound, and the values of a and b were obtained from eq 2 and are also given in Table 4.

Finally, calculated solubilities were compared with experimental values in Figures 3 and 4, using eq 3. Agreement between the calculated and experimental values for both compounds is fairly good. The Bartle method provided a good fit, with average absolute relative deviations of 5.9% for phenol and pyrocatechol. Therefore, solubilities can be confidently calculated at any temperature and pressure within the experimental range using eq 3 and the parameters of Table 4. Although only three temperatures were used in this correlation, previous works with data for a range of temperatures show that the correlation with temperature is valid.[8]

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