Solubilities of *p*-Quinone and 9,10-Anthraquinone in Supercritical Carbon Dioxide

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Equilibrium solubilities of *p*-quinone (1,4-benzoquinone) and 9,10-anthraquinone at 35 °C and 45 °C in supercritical carbon dioxide over a pressure range of about (85−300) bar have been measured using a supercritical fluid extractor coupled with a high-pressure liquid chromatography apparatus. The solubility results, along with those reported in the literature for 1,4-naphthoquinone, are correlated with a modified Peng−Robinson equation of state.

Introduction

In the past two decades supercritical fluids have been the focus of active research and development programs. The ability of a supercritical fluid to separate a multicomponent mixture is unique, since it utilizes the salient features of both distillation and liquid extraction. The solubility of a solute in a supercritical fluid is the most important thermophysical property that has to be determined and modeled for an efficient design of any extraction based on supercritical solvents.

A technique for measuring solubilities of organic solids in supercritical gases has been described in a previous work (Coutsikos et al., 1995). This technique is based on the coupling of a supercritical fluid extractor (sample preparation accessory manufactured by Thermo Separation Products), which prepares a sample extract, with a high-pressure liquid chromatography apparatus for an on-line sample analysis.

The reliability of the apparatus was preliminarily tested by measuring the solubilities of anthracene in supercritical carbon dioxide at 50 °C. The solubilities obtained were in good agreement with those reported by Johnston et al. (1982).

This method has also been used to determine solubility data of two aromatic alcohols (1-naphthol, hydroquinone) in supercritical carbon dioxide at various temperatures and pressures (Coutsikos et al., 1995).

Although the phase behavior of low-volatility organic compounds (alkanes, aromatic hydrocarbons, alcohols, phenols, acids) in supercritical fluids has been widely studied in recent years (Bartle et al., 1991), limited studies on the solubilities of solid aromatic ketones in supercritical fluids are reported in the literature. Schmitt and Reid (1986) have measured the solubilities of 1,4-naphthoquinone in four solvents (carbon dioxide, ethane, chlorotrifluoromethane, fluoroform), in a temperature range from (45 to 70) °C.

In this work the solubilities of *p*-quinone and 9,10-anthraquinone in supercritical carbon dioxide at 35 °C and 45 °C are measured over a pressure range of about (85−300) bar.

Experimental Section

The solubility measurements were carried out using a supercritical fluid extractor, the sample preparation accessory (SPA) manufactured by LDC Analytical (now named Thermo Separation Products), connected with a laboratory-assembled high-performance liquid chromatography (HPLC) apparatus, consisting of an ICI HPLC pump (model LC 1110), a Rheodyne injection valve, an APEX octadecyl symmetry reverse-phase column and an ICI LC 1200 UV/vis detector (wavelength range, 190−600 nm; wavelength accuracy, ±2 nm; wavelength reproducibility, ±0.2 nm). More details about the apparatus can be found elsewhere (Coutsikos et al., 1995).

Extraction Procedure and Quantitative Analysis. A sample of the solute is placed into a 5 mL stainless steel extraction cup with a porous bottom and top lid. The cup is placed into the extractor, which is located inside the oven of the SPA apparatus. When the system is charging, by means of a fluid pump, the carbon dioxide flows from the loop control valve through the recirulation pump and six-port valve into the extractor, which is loaded with the solute. A Sauvageau pressure gauge is connected to the outlet of the fluid pump, so that the digital pressure indication from the SPA would be converted into actual pressure units (bars). After leaving the extractor, the carbon dioxide stream is passed through a high-pressure cell of a variable wavelength UV detector. Once the desired pressure level has been reached, the extraction loop is isolated from the carbon dioxide supply tank, the recirculation pump is activated, and the fluid is allowed to flow through the closed loop. The progress of the extraction process is monitored by the UV detector. When this absorbance reading becomes constant with time, the equilibrium between the solid and the gaseous phase has been reached.

The injection of the sample extract (trapped inside a fixed volume sample loop of 10 μL) into the HPLC column is accomplished using a six-port injection valve and an eight-port one connected in tandem and controlled by a microprocessor. The passage of the sample extract through the HPLC detector provides a chromatogram peak, whose integration is performed using the appropriate software (JCL 6000 chromatography data system). Finally, the conversion of the obtained peak area to mass units of the solid solute is possible through a reference curve, established from standard solutions of known concentrations. A schematic diagram of the apparatus is shown in Figure 1.

Since the amount of the solid solute (m) dissolved in the supercritical fluid phase has been found (for a known volume V_{SL} equal to 10 μL), the corresponding solubility (mole fraction, y_2) at the specified conditions (temperature

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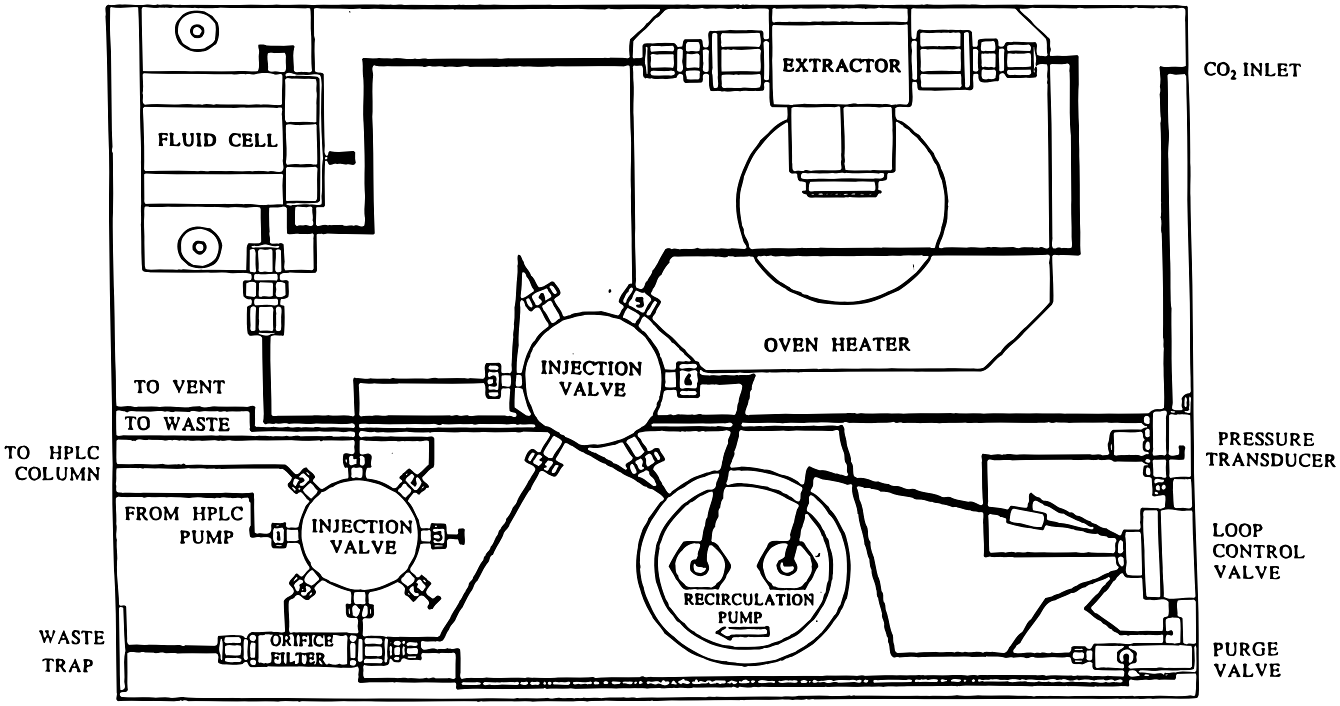

Figure 1. Schematic diagram of the supercritical fluid extractor.

Table 1. Sources, Purities, and Melting Points, T_m, of the Substances Used in This Work

substance	source	purity, mass %	T_m/K
carbon dioxide	Linde	99.995	
p-quinone	Merck	>98%	383−386
9,10-anthraquinone	Merck	>98%	555−558

Table 2. Solubility Data, y_2, of *p*-Quinone in Carbon Dioxide at 35 and 45 °C

t/°C	P/bar	$10^2 y_2$	P/bar	$10^2 y_2$
35	86.7	0.2945	173.6	1.9621
	95.1	0.6823	216.4	2.2267
	109.5	0.9275	259.3	2.3278
	121.8	1.1343	290.7	2.4822
	141.2	1.4432		
45	86.1	0.1064	186.6	2.3532
	97.4	0.5190	227.1	2.8588
	114.6	1.2246	264.4	3.0527
	126.4	1.5472	292.1	3.1421
	159.3	1.9477		

and pressure) of the experiment is calculated from the simple following relationship:

$$y_2 = \frac{m/\mathrm{MW}}{V_{\mathrm{SL}}/V_{\mathrm{CO_2}}} \qquad (1)$$

under the assumption that the mixture molar volume equals approximately the molar volume of the pure solvent ($V_{\mathrm{CO_2}}$) at the same temperature and pressure. MW is the molecular weight of the solid. The pure CO_2 density is calculated through the Bender EoS (1971) with the parameters reported by Luckas and Lucas (1989).

The above assumption that the mixture molar volume equals approximately the CO_2 molar volume is expected to be accurate for low mole fractions of the solute in the supercritical phase.

The injection of the sample extract is repeated several times at each pressure level, the average value of the peaks is recorded, and the pressure is adjusted to the next set point. The equilibrium pressure reading is within ±0.3%, while the temperature indication of the oven is within ±0.1 deg.

Table 3. Solubility Data, y_2, of 9,10-Anthraquinone in Carbon Dioxide at 35 and 45 °C

t/°C	P/bar	$10^5 y_2$	P/bar	$10^5 y_2$
35	84.1	0.1878	199.1	3.4072
	95.6	0.4705	239.2	4.0832
	116.4	1.0360	260.3	4.4547
	158.8	2.7707	298.2	5.1387
45	89.6	0.0882	219.5	5.0955
	107.7	0.3526	233.9	5.6133
	125.6	1.0315	262.1	5.9382
	141.4	1.6482	306.3	7.3992
	187.1	3.9025		

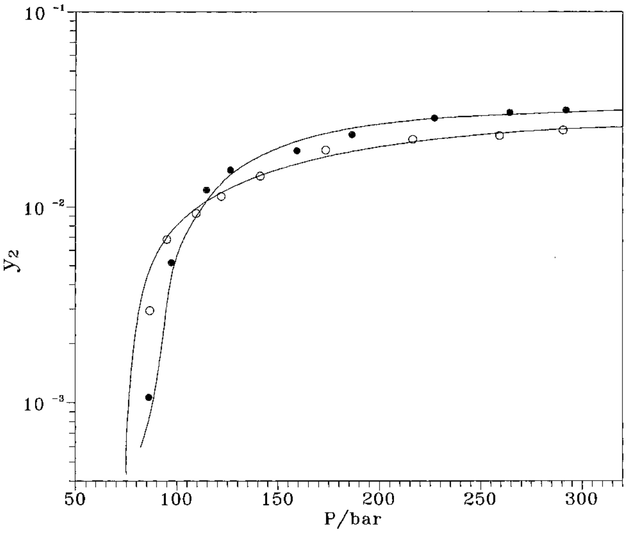

Figure 2. Solubility of *p*-quinone in carbon dioxide at different temperatures: (○) 35 °C; (●) 45 °C. (−) Solubility calculated with the two-parameter translated and modified Peng−Robinson EoS.

Materials. The carbon dioxide had a stated purity of 99.995 mass %. The *p*-quinone and 9,10-anthraquinone were purchased from Merck with a purity greater than 98 mass % (Table 1). The chemicals were used without any further purification.

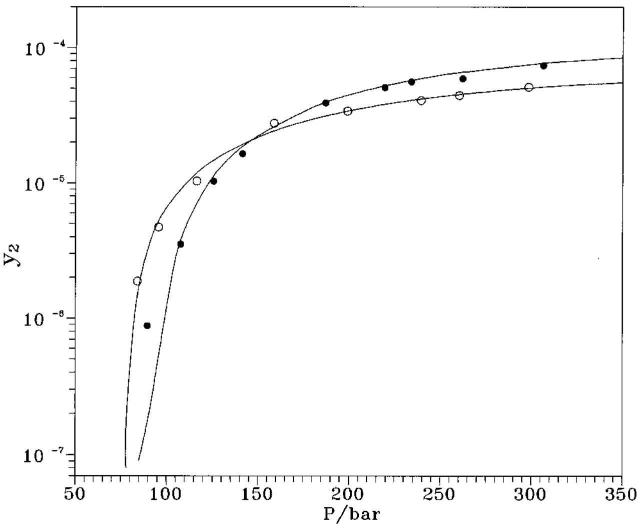

Figure 3. Solubility of 9,10-anthraquinone in carbon dioxide at different temperatures: (○) 35 °C; (●) 45 °C. (—) Solubility calculated with the two-parameter translated and modified Peng–Robinson EoS.

Table 4. Critical Properties (T_c, P_c) and Acentric Factors (ω) for the Compounds Considered in This Work

compound	T_c/K	P_c/bar	ω
carbon dioxide	304.19	73.81	0.228
p-quinone	747.33	50.02	0.424
1,4-naphthoquinone	877.50	40.67	0.572
9,10-anthraquinone	900.55	33.72	0.735

Table 5. Solid Vapor Pressures and Molar Volumes for the Compounds Considered in This Study

compound	t/°C	P^{sat}/Pa	V^S/cm^3 mol^{-1}
p-quinone	35	30.2434[a]	82.02
	45	65.3424[a]	
1,4-naphthoquinone	45	0.6891[b]	111.20
	55	1.9598[b]	
	70	8.3859[b]	
9,10-anthraquinone	35	6.52×10^{-5} [c]	145.20
	45	2.44×10^{-4} [c]	

[a] Coolidge and Coolidge (1927). [b] Schmitt and Reid (1986). [c] Bardi et al. (1973).

Experimental Results

Tables 2 and 3 present the solubilities of *p*-quinone and 9,10-anthraquinone in carbon dioxide, respectively, at two temperatures, 35 °C and 45 °C, over a pressure range from (84 to 306) bar. Those data are also shown graphically in Figures 2 and 3. Each reported datum is the average value of at least five injections of the sample extract to the HPLC column. The areas of the chromatogram peaks obtained for each equilibrium pressure level were reproducible within ±2%.

The reference curve for the *p*-quinone was established from eight standard solutions covering a concentration range from 0.28 g/L to 3.95 g/L. The HPLC solvent used was methanol, while the chromatograms were collected at 285 nm. The reference curve for 9,10-anthraquinone was established from eleven standard solutions covering a concentration range from 12.5 mg/L to 161 mg/L. The HPLC solvent used was methanol, and the wavelength of the HPLC detector was set to 254 nm.

The solubilities of the solutes increase with pressure, as the pressures are above the critical pressure of carbon dioxide. By observing the effect of the temperature on the solubilities, we find that the crossover region exists at pressures above 100 bar. For *p*-quinone, the crossover region is located at about 120 bar, and for 9,10-anthraquinone it is at about 150 bar.

The accuracy of the results is estimated to be about ±25% for $y \approx 10^{-5}$ and about ±10–15% for $y \approx 10^{-3}$–10^{-2}, which is in agreement with those reported in the literature for these levels (Johnston et al., 1982).

Thermodynamic Modeling

The solubilities of solids in supercritical fluids are given by

$$y_2 = \frac{P_2^{\mathrm{sat}} \exp[V_2^{\mathrm{S}}(P - P_2^{\mathrm{sat}})/RT]}{\varphi_2^{\mathrm{SCF}} P} \tag{2}$$

under the reasonable assumptions that no solvent dissolves in the solid phase and the solid solute is incompressible (Prausnitz, 1969). Subscript 2 refers to the solid solute and y_2 is the mole fraction of the solute in the fluid phase. Thus, if the solid-phase properties (molar volume, V_2^{S}, and solid vapor pressure, P_2^{sat}) are known, then the solubility of the solute in the supercritical solvent at any temperature, T, and pressure, P, can be calculated provided that an equation of state is available for the calculation of the fugacity coefficient, φ_2^{SCF}, of the solute in the supercritical fluid phase.

Correlation of the Solubility Data. Experimental data obtained in this work along with those found in the literature for 1,4-naphthoquinone, were correlated with the t-mPR cubic equation of state proposed by Magoulas and Tassios (1990), which is a translated and modified version of the original Peng–Robinson equation of state (Peng and Robinson, 1976).

The conventional van der Waals one-fluid mixing rules are employed for the cohesion and covolume EoS parameters along with the following combining rules:

$$a_{ij} = \sqrt{(a_{ii}a_{jj})}(1 - k_{ij}) \quad \text{and} \quad b_{ij} = \frac{1}{2}(b_{ii} + b_{jj})(1 - l_{ij}) \tag{3}$$

Table 6. Correlation of Solubility of Solids in Supercritical Carbon Dioxide with the Modified P–R Equation of State

compound	t/°C	P/bar	NDP	k_{ij}	% Δy[a]	k_{ij}	l_{ij}	% Δy[b]
p-quinone	35	86.7–290.7	9	0.1086	12.4	0.0902	−0.0363	9.5
	45	86.1–292.1	9	0.1064	26.8	0.0367	−0.1498	14.4
	35–45	86.1–292.1	18	0.1072	19.7	0.0688	−0.0732	12.1
1,4-naphthoquinone	45	101–363	6	0.1460	26	0.1088	−0.0822	19
	55	101–364	6	0.1487	28.6	0.1070	−0.090	17.5
	70	101–364	6	0.1528	32.8	0.0826	−0.1445	12.2
	45–70	101–364	18	0.1519	33.8	0.0899	−0.1284	15.7
9,10-anthraquinone	35	84.1–298.2	8	0.1079	11.2	0.0853	−0.0565	8.6
	45	89.6–306.3	9	0.1003	17.1	0.0625	−0.0929	12.4
	35–45	84.1–306.3	17	0.1039	18.2	0.0722	−0.0793	13.1

[a] One-parameter correlation. [b] Two-parameter correlation.

where k_{ij} and l_{ij} are binary interaction coefficients which account for the solute−solvent energetic interactions and size and shape differences, respectively. The solid solutes involved in this study are presented in Table 4, along with their critical properties (T_c, P_c) and acentric factors. The critical properties have been estimated by using the Joback−Reid group contribution method (1987), while the acentric factors were estimated using the Lee−Kesler method. The normal boiling point (T_b) values for *p*-quinone and 1,4-naphthoquinone were also estimated through the Joback−Reid method, while for 9,10-anthraquinone the experimental T_b value has been used. Molar volumes and sublimation pressures of the solids considered in this study are presented in Table 5.

Detailed correlation results using the modified Peng−Robinson EoS are presented in Table 6 along with the optimum values for the binary interaction coefficients k_{ij} and l_{ij}.

Conclusions

In this work, solubilities of two aromatic ketones (with two C=O groups) 1,4-benzoquinone (*p*-quinone) and 9,10-anthraquinone in supercritical carbon dioxide have been measured.

The solubility data are correlated with a modified and translated Peng−Robinson EoS using either one adjustable parameter (k_{ij}) or two adjustable parameters (k_{ij} and l_{ij}). As was expected, the two-parameter correlation of the solubility data is superior than the one-parameter correlation. The results are very good for temperature-dependent parameters and satisfactory for temperature-independent ones.

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