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Solubilities of Some 1,4-Dihydroxy-9,10-anthraquinone Derivatives in Supercritical Carbon Dioxide

Mohammad Reza Fat'hi,[†] Yadollah Yamini,[†] Hashem Sharghi,[‡] and Mojtaba Shamsipur*[,§]

Department of Chemistry, Tarbiat Modarres University, Tehran, Iran, Department of Chemistry,
Shiraz University, Shiraz, Iran, and Department of Chemistry, Razi University, Kermanshah, Iran

The equilibrium solubilities of three recently synthesized 9,10-anthraquinone derivatives have been measured in supercritical carbon dioxide using a simple and reliable static method. The measurements were performed in the pressure range 121.6 to 405.3 bar at temperatures (35, 45, 55, 65, and 75) °C. The measured solubilities were correlated using the model proposed by Chrastil. The calculated results show good agreement with the experimental data.

Introduction

In the past decades widespread attention has been paid to supercritical fluid extraction (SFE) as an interesting alternative to conventional extraction methods (Bartle et al., 1991). Industrial supercritical extraction processes are now well-established (Johnson and Penninger,1989); for example, the technique is used on a large scale for coffee decaffeination and on a smaller scale for the extraction of natural products such as perfumes (Moyler, 1989), as well as in food processing (Palmer and Ting, 1995). The most widely used supercritical fluid is carbon dioxide because it is nontoxic, nonflammable, and relatively inexpensive and possesses reasonable critical properties as well as a high solvent power for a wide range on nonpolar and intermediately polar organic compounds (Bartle et al., 1991). Information on solubilities in supercritical fluids is perhaps the most important thermophysical property that must be determined and modeled in order to efficiently design the extraction procedures based on supercritical solvents.

9,10-Anthraquinones as the largest group of naturally occurring quinones are of great importance both in industry and in medicine (Thomson, 1971). In addition to a wide variety of chemical and industrial applications (Dadfarnia et al., 1993; Gutierrez and Nguyen, 1988; Thomson, 1971), recently the synthetic derivatives of anthraquinones, as well as naturally occurring derivatives, have been used for medical purposes (Gutierrez and Nguyen, 1988).

This work was undertaken to determine the solubilities of three 1,4-dihydroxy-9,10-anthraquinone derivatives, recently synthesized in this research group (Khojasteh, 1994), in supercritical carbon dioxide over a wide range of temperatures and pressures. The measured solubilities were nicely correlated using the model proposed by Chrastil (1982).

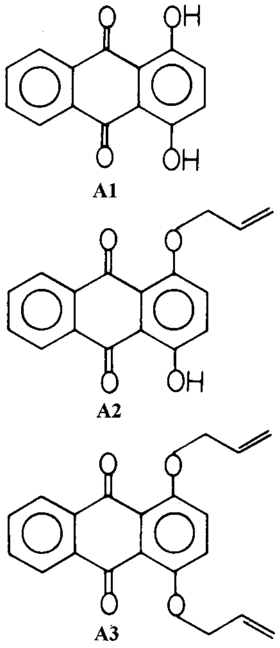

Figure 1. Structure of anthraquinones.

Experimental Section

HPLC-grade methanol (Aldrich) was used as received. Pure carbon dioxide (Sabalan, Tehran, 99.99%) was used for all extractions. Reagent grade 1,4-dihydroxy-9,10-anthraquinone (A1, Merck) was of the highest purity available and was used as received. 1-Hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (A2) and 1,8-bis(prop-2′-enyloxy)-9,10-anthraquinone (A3) were synthesized (Khojasteh, 1994) and used after recrystallization from reagent-grade benzene (Merck) and vacuum-drying. Structures of the anthraquinone derivatives used are shown in Figure 1.

A Suprex MPS/225 integrated SFE-SFC system modified for the solubility determination in SFE mode was used. A schematic diagram of the modified static system used is shown in Figure 2. Solubility measurements were accomplished with a 1-mL extraction vessel in the pressure range from 121.6 to 405.3 bar at temperatures (35, 45, 55, 65, and 75) °C for a duration of 15 min. The solid solutes (100−200 mg) were mixed well with some 1 g of glass beads and packed into the extraction vessel. This procedure prevents channeling, increases the contact surface between the sample and the supercritical fluid, and, consequently,

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[†] Tarbiat Modarres University.
[‡] Shiraz University.
[§] Razi University.

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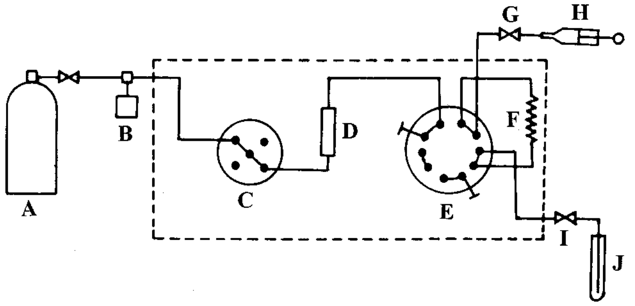

Figure 2. Schematic diagram of experimental apparatus for measuring solubilities: (A) CO_2 gas tank; (B) supercritical fluid pump; (C) 5-port, 4-position valve; (D) 1-mL equilibrium cell; (E) 10-port, 2-position valve; (F) injection loop; (G) on/off valve; (H) syringe; (I) microadjust valve; (J) collection vial.

Table 1. Solubility of Naphthalene in Supercritical Carbon Dioxide at 35 °C

	10^3y			
P/bar	this work	Reverchon et al., 1993	Iwai et al., 1991	Kurnik and Reid, 1982
138	15.2	13.9	14.1	16.2
168	16.2		16.5	17.6
204	17.4		17.6	18.8

reduces the equilibration time. Sintered stainless steel filters (5 μm) were used to prevent any carryover of the solutes. Supercritical CO_2 was pressurized and passed into the vessel D through the five-port, four-position valve C. After equilibrium at the desired temperature and pressure was reached (for about 15 min), a 122-μL portion of the saturated supercritical CO_2 was loaded into injection loop F by means of a 10-port, 2-position valve E. Then the loop was depressurized into the collection vial J containing a known volume of methanol by switching the injection valve E. To prevent solvent dispersal, the depressurizing rate of the sample loop was adjusted by the valve I. Finally, the G and I valves were opened completely, and the sample loop was washed with some methanol and collected into the collection vial J. The equilibrium temperature and pressure were measured to an accuracy of ±1 °C and ±0.5 bar, respectively.

The solubilities were calculated by absorbance measurements at λ_{max} of each compound using a model 2100 Shimadzu UV−vis spectrophotometer. The stock solutions of the compounds A1−A3 (100 $\mu g \cdot cm^{-3}$) were prepared by dissolving appropriate amounts of the solid samples in methanol. A set of standard solutions was then prepared by appropriate dilution of the stock solutions. The calibration curves obtained (with regression coefficients better than 0.999) were used to establish the concentration of the anthraquinone derivatives in the collection vial. The mole fractions of the solutes were generally reproducible within ±3%.

Results and Discussion

The reliability of the apparatus was preliminarily checked by measuring the solubilities (mole fraction, *y*) of naphthalene in supercritical CO_2 at 35 °C, and the results are summarized in Table 1. The values given in Table 1 are obtained from an arithmetic average of three replicate measurements with relative standard deviations less than 3%. As seen, the results are in satisfactory agreement with those reported before (Iwai et al., 1991; Kurnik and Reid, 1982; Reverchon et al., 1993).

Table 2. Solubilities of 1,4-Dihydroxy-9,10-anthraquinone (A1), 1-Hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (A2), and 1,8-Bis(prop-2′-enyloxy)-9,10-anthraquinone (A3) in Supercritical Carbon Dioxide

		A1		A2		A3	
P/bar	ρ/g·dm^{-3}	10^5y	s/g·dm^{-3}	10^5y	s/g·dm^{-3}	10^5y	s/g·dm^{-3}
			t = 35 °C				
121.6	770	4.0	0.17	4.9	0.24	6.6	0.37
162.1	833	5.4	0.24	5.1	0.27	8.7	0.52
202.7	871	6.1	0.29	7.0	0.39	10.5	0.66
243.2	898	7.5	0.37	8.3	0.47	12.9	0.84
283.7	922	7.9	0.40	10.5	0.62	14.5	0.98
324.2	942	9.0	0.47	11.7	0.71	16.7	1.05
364.8	960	10.4	0.54	12.8	0.78	18.2	1.17
405.3	975	11.1	0.59	13.1	0.81		
			t = 45 °C				
121.6	665	2.4	0.08	5.0	0.27	3.2	0.14
162.1	763	4.6	0.19	7.5	0.54	5.6	0.27
202.7	815	6.4	0.29	11.2	0.66	7.9	0.41
243.2	852	8.3	0.39	11.6	0.72	10.4	0.56
283.7	880	10.1	0.48	13.3	0.85	12.3	0.69
324.2	905	12.0	0.59	14.8	0.97	14.8	0.86
364.8	924	13.0	0.65	16.7	1.13	16.6	0.97
405.3	945	14.4	0.75			17.9	1.09
			t = 55 °C				
121.6	524	1.7	0.05	2.1	0.07	2.6	0.11
162.1	685	4.5	0.17	5.9	0.26	3.9	0.30
202.7	757	7.4	0.30	9.6	0.47	8.5	0.47
243.2	805	10.3	0.45	13.0	0.67	12.4	0.73
283.7	838	13.0	0.60	17.1	0.91	16.1	0.98
324.2	867	15.1	0.71	19.7	1.08	19.0	1.20
364.8	889	17.2	0.83	24.3	1.37	22.0	1.42
405.3	909	18.7	0.93				
			t = 65 °C				
121.6	397	1.6	0.03	0.9	0.02	0.8	0.02
162.1	601	5.0	0.16	4.6	0.18	7.6	0.33
202.7	695	8.7	0.33	94	0.41	11.7	0.59
243.2	754	12.7	0.52	14.7	0.71	12.8	0.70
283.7	796	15.8	0.69	20.1	1.20	15.8	0.92
324.2	828	18.9	0.85	25.8	1.36	20.0	1.20
364.8	854	22.0	1.02	31.4	1.71		
405.3	876	24.9	1.19	35.8	1.99		
			t = 75 °C				
121.6	328	1.3	0.02	1.0	0.02	0.2	0.01
162.1	519	3.6	0.10	3.9	0.13	3.9	0.15
202.7	631	8.2	0.28	10.5	0.42	10.0	0.46
243.2	702	13.5	0.52	18.8	0.84	11.6	0.59
283.7	750	18.0	0.74	27.2	1.30	13.8	0.75
324.2	788	22.2	0.95	34.8	1.75	14.0	0.80
364.8	818	26.6	1.19	42.5	2.22		
405.3	843	31.4	1.44	49.8	2.67		

The solubilities of the compounds at temperatures (35, 45, 55, 65, and 75) °C and in the pressure range from 121.6 to 405.3 bar were determined. The resulting solubilities in terms of equilibrium mole fraction, *y*, of the solute and in grams per liter, *s*, of the solute in supercritical carbon dioxide are summarized in Table 2. Each reported solubility is the average value of three replicate samples.

Examination of the solubility data in Table 2 reveals that the solubility of the solutes increases with increasing pressure at constant temperature, the influence of pressure on the solubilities being more pronounced at higher temperatures. This is in accord with the conventional wisdom stating that the density of a supercritical fluid must increase in order to increase the solubility and extraction efficiency (Miller and Hawthorne, 1995).

From the effect of temperature on solubilities (Table 2), it is found that the retrograde solubility (crossover/pressure effect) behavior for the compounds exists in the supercritical state, as it was reported for different organic compounds previously (Knez et al., 1995; Tsai and Tsai, 1995; Yu et al., 1995). At pressures above the crossover point (i.e.,

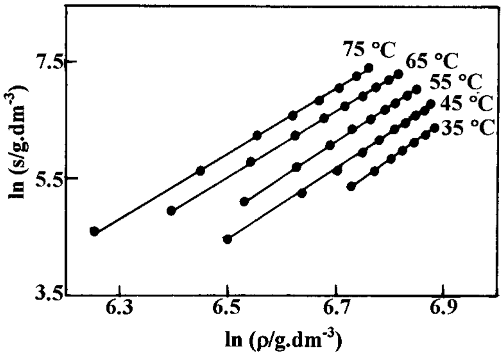

Figure 3. Plot of solubility against density of supercritical CO_2 for A1.

Table 3. Solubility Constants of the Chrastil Model for A1−A3 in Supercritical CO_2

anthraquinone	k	a	b
A1	5.94	−4689	20.9
A2	6.08	−5715	24.3
A3	4.29	−2972	16.0

about 202.7 bar), solubilities increase with increases of both pressure and temperature, while below this point, solubilities increase with increasing pressure but decrease with an increase in temperature. The observed different effects of temperature on solubilities of compounds A1−A3 could be due to the influences of temperature on such diverse properties of the system as the solute vapor pressure, the solvent density, and the intermolecular interactions in the supercritical fluid phase. At lower pressures, the fluid density is lowered by small increases in temperature. Since the density effect predominates at this region, the solubility will decrease with increasing temperature. However, at higher pressures, the fluid density is less dependent on temperature so that the observed increase in solubility with temperature could be primarily due to other factors, especially the higher vapor pressure of the solid samples.

The experimental solubility data for the anthraquinones were correlated using the model proposed by Chrastil (1982). This model is based on the hypothesis that each molecule of a solute (S) associates with k molecules of supercritical solvent (C) to form a solvato complex (SC_k), which is in equilibrium with the gas. The model proposes a linear relationship between the logarithm of the solubility, s, and the logarithm of fluid density, ρ, as follows

$$\ln(s/\text{g}\cdot\text{dm}^{-3}) = k\ln(\rho/\text{g}\cdot\text{dm}^{-3}) + a/T + b \qquad (1)$$

where $a = \Delta H/R$ and $b = -\ln\,[M_C{}^k/(M_S + kM_C)] + q$, s is the solubility, ρ is the fluid density, T is the temperature, k is the dissociation number, ΔH is the total enthalpy of reaction (i.e., enthalpy of solvation plus enthalpy of vaporization of the solute), q is a constant, and M_S and M_C are the molecular weights of the solute and solvent, respectively. Ln s is a linear function of $1/T$ at constant density. The value of b can be chosen to minimize the deviation of the model from experimental data.

The solubility data obtained in this study show the expected linear relationship predicted by the Chrastil model. Sample plots of ln s vs ln ρ for compound A1 at various temperatures are shown in Figure 3. The straight lines reported in Figure 3 are the best fit of eq 1 to the solubility data. The slopes of the solubility isotherms are within a good approximation equal. The optimum calculated values of k, a, and b for solutes A1−A3 are given in Table 3.

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