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Solubilities of Some Aminoanthraquinone Derivatives in Supercritical Carbon Dioxide

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The equilibrium solubilities of four recently synthesized aminoanthraquinones in supercritical CO_2 have been measured over a temperature range of 308 to 358 K and a pressure range of 122 to 358 bar, using a simple static method. The solubility data were correlated by a semiempirical model. The calculated results show satisfactory agreement with the experimental data.

Introduction

Conventional dyeing of polyester fabrics requires a large amount of water and also discharges much wastewater. Because of environmental problems such as the emission of organic materials in wastewater, a new dyeing process has been developed in which supercritical carbon dioxide is used as a solvent for the dyes.[1,2] The advantages of supercritical carbon dioxide are that it can be recycled; it is inexpensive, essentially nontoxic, and nonflammable; and it has easily accessible critical conditions. Moreover, the dyes can be more usefully utilized, because all of the dye dissolved in the supercritical fluid can be recovered when the fluid is expanded.

To develop and design the supercritical dyeing processes, dye solubility data are necessary. Some researchers have reported extensive measurements of the solubility of disperse dyes in supercritical carbon dioxide.[3−10] Disperse dyes usually used for the dyeing of polyester textiles are divided into two main groups, i.e., azo-dyes and anthraquinone derivatives. In recent years, we have reported the solubilities of some 9-10-anthraquinone,[11,12] hydroxyxanthone,[13] and 9-anthrone drivatives[14] in supercritical carbon dioxide. In this study, the solubility of the four recently synthesized anthraquinone derivative disperse dyes i.e., 1-amino-2-methyl-9,10-anthraquinone (A1), 1-amino-2-ethyl-9,10-nthraquinone (A2), 1-amino-2,3-dimethyl-9,10-anthraquinone (A3), and 1-amino-2,4-dimethyl-9,10-anthraquinone (A4) in supercritical carbon dioxide have been measured over a wide range of pressure and temperature. The measured solubilities were nicely correlated using a semiempirical model proposed by Bartle et al.[15]

Experimental Section

HPLC-grade methanol (Merck) was used as received. CO_2 (99.99%) was purchased from Sabalan Gas Co. (Tehran, Iran). The aminoanthraquinone derivatives A1−A4 were synthesized[16] and used after recrystallization from reagent grade benzene (Merck) and vacuum-drying. The purities (>99.9%) of aminoanthraquinone derivatives were confirmed by spectroscopic data and elemental analysis. The structures of the aminoanthraquinone derivatives studied are shown in Figure 1.

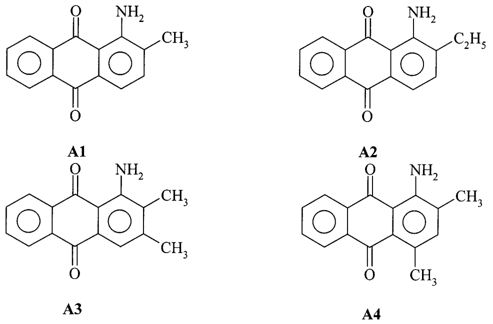

Figure 1. Structures of Aminoanthraquinone Derivatives.

A Suprex MPS/225 integrated SFE/SFC system equipped with a modified static system for the solubility determination in the SFE mode was used. A detailed description of the apparatus and operating procedure is given elsewhere.[11,12] Solubility measurements were accomplished with a 1 mL extraction vessel in the pressure range from (122 to 355) bar at the temperatures (308, 318, 328, 338, 348, and 358) K for a duration of 30 min. It should be noted that, by monitoring the solubility data versus time, 30 min was found to be adequate to ensure the attainment of equilibrium. The solid solutes (100 mg) were mixed well with glass beads and packed into the extraction vessel. This procedure increases the contact surface between the sample and the supercritical fluid and, consequently, reduces the equilibration time. Supercritical CO_2 was pressurized and passed into the extraction vessel. After equilibrium at the desired temperature and pressure was reached, a 132 μL portion of the saturated supercritical CO_2 was loaded into the injection loop. Next the loop was depressurized into a collection vial containing methanol. Finally, the sample loop was washed with the methanol, which was collected in the collection vial. The final volume of the solution was 5 mL.

The solutbilities were calculated by fluorescence measurements using a LS 50B Perkin-Elmer Luminescence spectrofluorimeter. Excitation and emission wavelengths of 474 and 579.4 nm, respectively, were used for the quantitative determinations.

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Table 1. Solubilities of Aminoanthraquinone Derivatives A1−A4 in Supercritical Carbon Dioxide

			A1		A2		A3		A4	
T/K	P/bar	ρ/kg·M^{-3}	$10^5\,y$	s/g·L^{-1}	$10^5\,y$	s/g·L^{-1}	$10^5\,y$	s/g·L^{-1}	$10^5\,y$	s/g·L^{-1}
308	122	771	1.90	0.8	1.58	0.07	0.51	0.24	2.07	0.009
	152	818	2.45	0.11	2.15	0.10	0.52	0.25	2.54	0.012
	182	850	3.08	0.14	2.55	0.12	0.34	0.31	3.62	0.018
	213	876	3.84	0.18	3.15	0.16	0.61	0.35	5.04	0.025
	243	897	4.17	0.20	3.35	0.17	0.89	0.38	5.62	0.029
	274	916	4.50	0.22	3.56	0.19	0.97	0.42	6.00	0.031
	304	931	4.62	0.23	3.61	0.19	1.08	0.47	6.55	0.035
	334	946	4.81	0.25	3.82	0.21	1.05	0.54	6.55	0.035
	355	955	5.51	0.28	3.91	0.21	1.18	0.55	7.02	0.038
318	122	661	1.48	0.05	1.29	0.05		0.16		
	152	745	2.30	0.09	2.03	0.09	1.17	0.24		
	182	792	3.06	0.13	2.75	0.12	1.30	0.33		
	213	826	3.99	0.18	3.20	0.15	1.61	0.40		
	243	852	4.72	0.22	3.63	0.18	1.81	0.49		
	274	875	4.93	0.23	3.83	0.19	1.97	0.55		
	304	893	5.38	0.26	4.03	0.21	2.20	0.61		
	334	910	5.62	0.28	4.31	0.22	2.30	0.69		
	355	919	6.12	0.30	4.41	0.23	2.10	0.74		
328	122	516	0.80	0.02	0.89	0.03	0.54	0.12	0.02	0.000
	152	657	1.76	0.06	1.79	0.07	1.22	0.19	2.13	0.008
	182	726	2.76	0.11	2.75	0.11	1.56	0.30	3.73	0.016
	213	771	3.87	0.16	3.74	0.16	2.05	0.41	5.04	0.022
	243	804	4.97	0.22	4.48	0.21	2.33	0.50	6.07	0.028
	274	831	5.83	0.26	5.22	0.25	2.71	0.64	6.78	0.032
	304	853	7.93	0.36	5.70	0.28	3.02	0.72	7.77	0.038
	334	872	8.68	0.41	6.03	0.30	3.35	0.81	9.49	0.047
	355	884	9.07	0.43	6.07	0.31	3.66	0.94	9.74	0.049
338	122	396	0.46	0.01	0.26	0.01		0.08	0.02	0.000
	152	561	1.28	0.04	1.71	0.05	0.58	0.17	0.51	0.002
	182	654	2.49	0.09	2.97	0.11	1.14	0.29	3.59	0.013
	213	712	3.74	0.14	4.07	0.17	1.54	0.43	5.42	0.022
	243	754	4.99	0.20	5.00	0.22	2.11	0.58	7.25	0.031
	274	786	6.04	0.26	5.76	0.26	2.56	0.68	8.91	0.040
	304	812	6.68	0.29	5.10	0.24	3.16	0.88	9.59	0.045
	334	834			4.37	0.21	3.56	1.01	11.21	0.054
	355	848			4.36		3.79	1.10	11.97	0.058
348	122	327	0.48	0.01	0.13	0.00		0.08	0.02	0.000
	152	477	1.56	0.04	1.35	0.04		0.13	0.02	0.000
	182	585	3.05	0.10	3.09	0.10	0.46	0.26	0.03	0.000
	213	652	4.33	0.15	4.46	0.17	1.63	0.43	3.73	0.014
	243	702	5.49	0.21	5.99	0.24	2.52	0.60	10.19	0.041
	274	740	8.31	0.33	6.98	0.29	3.44	0.75	16.60	0.070
	304	772	9.52	0.40	7.78	0.34	3.92	1.03	20.59	0.091
	334	796	10.14	0.44			4.39	1.24	23.94	0.109
	355	811	10.96	0.48			4.60	1.42	25.98	0.121
358	122	287							0.03	
	152	406							0.02	
	182	517							2.68	0.008
	213	593							8.66	0.029
	243	650							15.12	0.056
	274	693							18.49	0.073
	304	728							22.35	0.093
	334	757							24.37	0.106
	355	774							24.70	0.109

The stock solutions of compounds A1−A4 (500 μg·mL^{-1}) were prepared by dissolving appropriate amounts of the solid samples in methanol. A set of standard solutions was then prepared in the range 0.5 to 5 μg·mL^{-1} by appropriate dilution of the stock solutions. The calibration graphs obtained (with regression coefficient better than 0.998) were used to established the concentration of the aminoanthraquinone derivatives in the collection vial. The results were used to calculate the mole fraction solubilities of solutes in supercritical carbon dioxide, y. The solubilities measured were generally reproducible within ±5% (given as standard deviation on at least three replicated measurements).

Results and Discussion

The reliability and efficiency of the solubility measurement technique were previously established by measuring the solubility of naphthalene in supercritical CO_2 at 308 K and different pressures, as described before.[11,12]

Table 1 summarizes the solubilities of aminoanthraquinones A1−A4 at different temperatures and pressures. The experimental results are listed in terms of the equilibrium mole fraction of solute, y, and equilibrium solubility, s/g·L^{-1}, of the solute in supercritical carbon dioxide. Each reported datum is the average of at least three replicate sample measurements. The mole fraction solubilities of the solutions were reproducible within ±5%.

From the data given in Table 1, it is seen that the solubility of compounds A1−A4 increases with increasing pressure at constant temperature, with the influence of pressure on the solubilities being more pronounced at higher temperatures. This is despite the fact that the density of CO_2 decreases at higher temperatures.

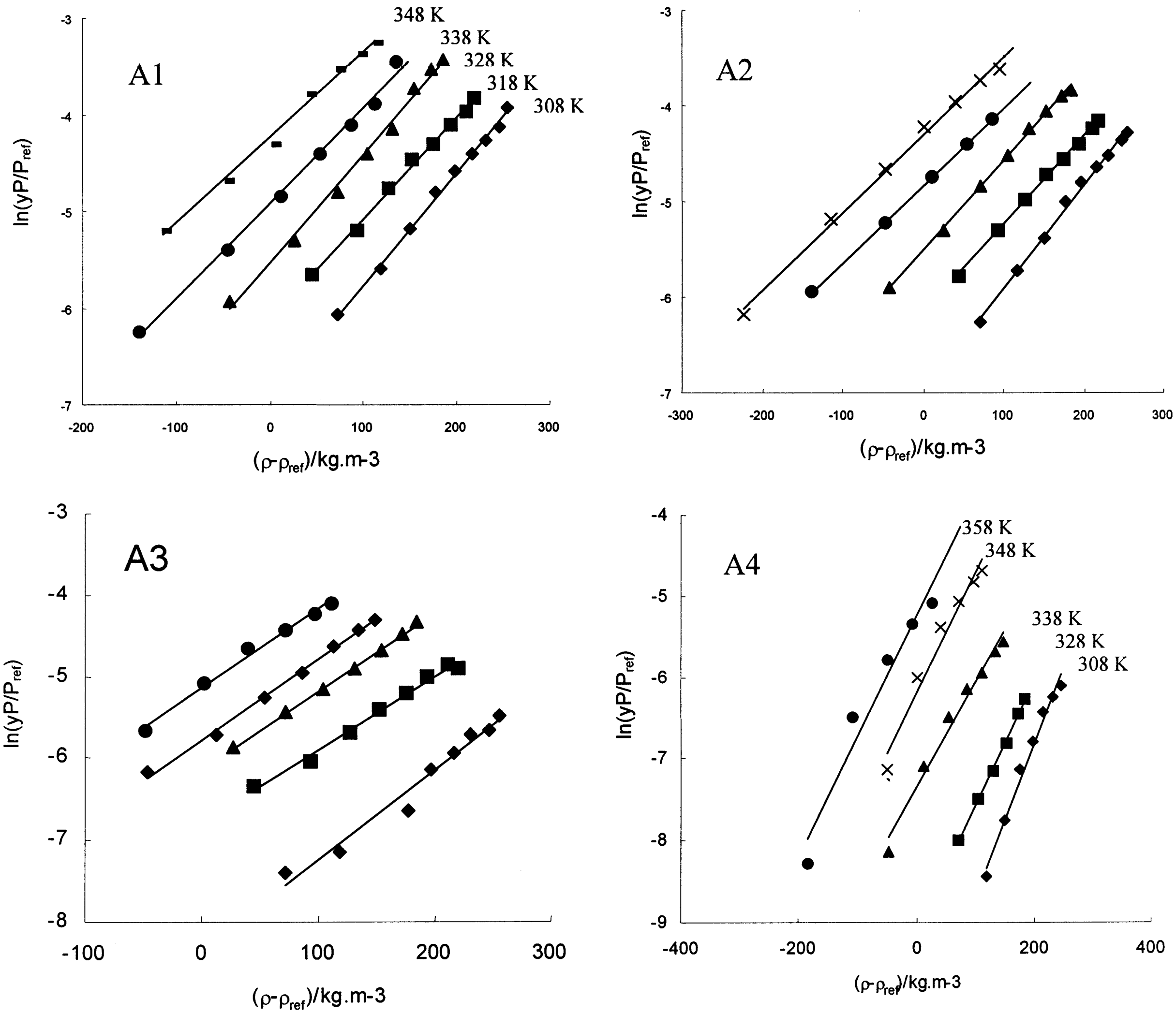

Figure 2. Plots of $\ln(yP/P_{\mathrm{ref}})$ versus $(\rho - \rho_{\mathrm{ref}})$ for A1–A4.

By examining the effect of the temperature on the solubility data (Table 1), it can be observed that relatively sharp crossover regions exist at about 210 bar for A1, 150 bar for A2, 180 bar for A3, and 210 bar for A4. Such a retrograde (crossover versus pressure effect) behavior has already been reported for different organic compounds.[7–9,11–13,17,18]

At pressures that are less than the crossover region, solvent densities are decreased by small increases in temperature; because the density effect is dominant in this region, the solubility will decrease with rising temperature. At higher pressures, the solvent density is less dependent on temperature, so that the increase in solubility is primarily due to the higher vapor pressure of the solid. On the other hand, no change was observed in the excitation and emission spectra of the extracted samples in a temperature range (308 to 348) K, which supports the stability of the aminoanthraquinone derivatives under these conditions.

The results obtained in this study indicate that the solubilities of aminoanthraquinone derivatives vary in the order of A3 > A1 > A2 ≫ A4. The melting points of A1, A2, A3, and A4 are (475, 432, 469, and 485) K, respectively.

The results from the present study were correlated by a simple semiempirical equation proposed by Bartle et al.[15]

$$\ln(yP/P_{\mathrm{ref}}) = A + C\,(\rho - \rho_{\mathrm{ref}}) \tag{1}$$

Table 2. Solubility Constants *a*, *b*, and *C* and Estimated $\Delta_{\mathrm{sub}}H$, kJ/mol

compound	a	b/K	C/M^3·kg^{-1}	$\Delta_{\mathrm{sub}}H$/kJ·mol^{-1}
A1	14.3	−6478	0.0104	53.85
A2	14.5	−6540	0.0091	54.37
A3	16.6	−7526	0.0098	62.57
A4	15.9	−7632	0.0102	65.1

where

$$A = a + b/T \tag{2}$$

and

$$\ln(yP/P_{\mathrm{ref}}) = a + b/T + C(\rho - \rho_{\mathrm{ref}}) \tag{3}$$

Here, P_{ref} is a standard pressure of 1 bar and ρ_{ref} is a reference density for which a value of 700 kg·m^{-3} was used. The other terms in the above equations have already been discussed.[19–21]

From the experimental data, each isotherm was fitted using eq 1 to obtain the values of A and C (Figure 2). The values of C were then averaged for each compound (Table 2).

By holding C at its average value, the experimental solubility data were then used to evaluate the A values at various temperatures for each aminoanthraquinone. The plots of A versus $1/T$ for each compound resulted in a

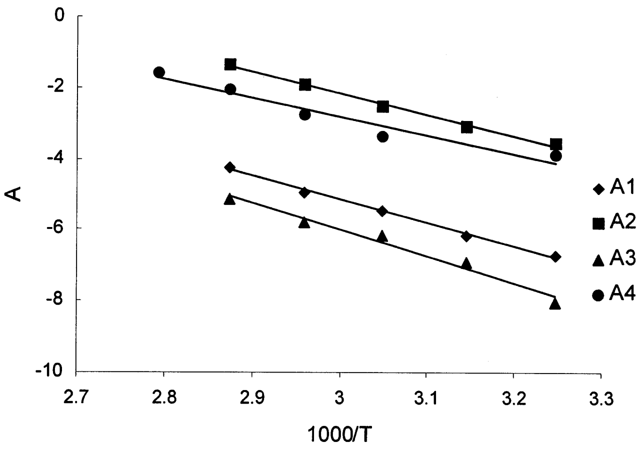

Figure 3. Plots of A versus $1/T$ for A1−A4.

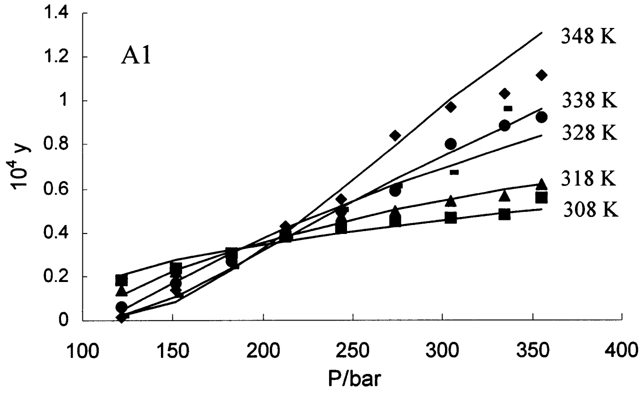

Figure 4. Comparison of experimental (points) and calculated (lines) solubilities at various temperatures for A1.

straight line (Figure 3) from which the intercept a and slope b were obtained. The resulting a and b values for different compounds are also included in Table 2. Finally, the values of a, b, and C were used to predict solubility from eq 3. Figure 4 compares the calculated isotherms with the experimental data for A1. As seen, the agreement is satisfactory. The parameter b is approximately related to the enthalpy of sublimation of the solid solute, $\Delta_{\text{sub}}H$ by[22]

$$\Delta_{\text{sub}}H = -Rb \tag{4}$$

where R is the gas constant. The estimated $\Delta_{\text{sub}}H$ values are also included in Table 2.

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