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Solubilities of 2,2′-Bipyridine and 4,4′-Dimethyl-2,2′-bipyridine in Supercritical Carbon Dioxide

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The solubilities of 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine in supercritical carbon dioxide were measured at temperatures from (308 to 323) K and pressures from (8.1 to 25.9) MPa. The measured solubilities were correlated using a semiempirical model and differed from the measured values by between (4.6 and 34.4) %.

Introduction

Carbon dioxide is a solvent of choice in supercritical fluid extraction (SFE) because it is inexpensive, nontoxic, and readily available in relatively pure form and has moderate critical constants (7.38 MPa and 31.1 °C). Unfortunately, direct extraction of metal ions by supercritical CO_2 is highly inefficient because of the charge neutralization requirement and the weak solute−solvent interactions. The use of supercritical CO_2 containing chelating agents is an attractive technique for the remediation of metal-contaminated wastes or the extraction of high-value metals.[1−3] However, when metal ions are bound to an organic ligand, they may become quite soluble in supercritical CO_2.[4−6] It is well-known that bipyridine is a strong chelating agent and can form stable complexes with almost all heavy metal ions.[7] As a result, it is desired to develop an effective method for extraction metals with bipyridine in supercritical CO_2. However, prior to extraction of metal ions, accurate solubility data of bipyridine are needed. Although a large of number of studies have been performed on solubilities of many compounds in supercritical CO_2, little is known about bipyridines.

In the present work, solubilities of 2,2′-bipyridine (Bpy) and 4,4′-dimethyl-2,2′-bipyridine (DMBP) in supercritical CO_2 over the pressure range of (8.1 to 25.9) MPa and at temperatures of (308, 313, 318, and 323) K were determined, and the measured solubilities were also correlated using a semiempirical model.

Experimental Section

Chemicals. CO_2 with a mass fraction purity of 99.99 % was obtained from Wuhan Steel Co., and Bpy was obtained from China National Medicines Corporation with a minimum stated mass fraction purity of ≥ 99.5 %. DMBP was supplied by Aldrich with a stated mass fraction purity of 99 %. All compounds were used without further purification.

Solubility Apparatus. Solubility measurement was carried out in a stainless steel view cell (7.11 mL) with two sapphire windows, which permitted visual observation of the phase behavior. The compounds in the cell were stirred by a magnetic stirrer. The temperature was controlled using a temperature controller jacket with an uncertainty of better than ± 0.05 K. A “JASCO PU-1580-CO_2” CO_2 delivery pump was used to cool and deliver CO_2 fluid, and a “JASCO BP-1580-81” back pressure regulator was used to maintain the pressure constant

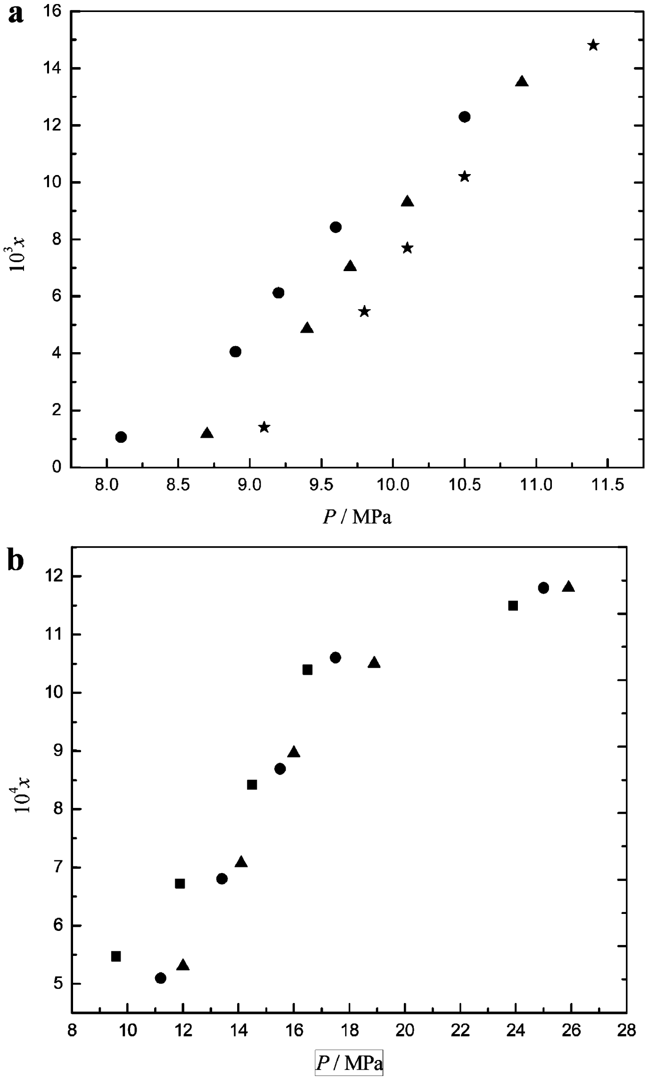

Figure 1. Solubilities of compounds in supercritical CO_2: panel a, Bpy; panel b, DMBP. ■, 308 K; ●, 313 K; ▲, 318 K; ★, 323 K.

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Table 1. Solubility at Temperature T, Density ρ, and Mole Fraction x for (Bpy + DMBP)

	Bpy					DMBP				
T/K	P/MPa	ρ/kg·m^{-3}	10^3x	10^3x_{calcd}	AAD/%	P/MPa	ρ/kg·m^{-3}	10^4x	10^4x_{calcd}	AAD/%
308						9.6 ± 0.1	710	5.47	5.01	8.410
						11.9 ± 0.1	760	6.72	6.28	6.548
						14.5 ± 0.2	805	8.42	7.67	8.907
						16.5 ± 0.1	835	10.4	8.79	15.48
						23.9 ± 0.1	890	11.5	9.86	14.26
										10.559
313	8.1 ± 0.2	389	1.07	1.36	27.10	11.2 ± 0.1	699	5.09	5.50	8.055
	8.9 ± 0.1	488	4.06	3.36	17.24	13.4 ± 0.2	750	6.80	7.22	6.176
	9.2 ± 0.2	530	6.13.	4.96	19.09	15.5 ± 0.1	785	8.69	8.50	2.186
	9.6 ± 0.1	590	8.43	8.70	3.203	17.5 ± 0. 2	818	10.6	10.1	4.717
	10.5 ± 0.2	660	12.3	16.1	30.89	25.0 ± 0.2	878	11.8	12.0	1.695
					19.505					4.566
318	8.7 ± 0. 5	360	1.16	2.00	72.41	12.0 ± 0.2	652	5.30	4.74	10.57
	9.4 ± 0.3	410	4.85	3.08	36.49	14.1 ± 0.1	722	7.07	7.49	5.941
	9.7 ± 0.2	454	7.03	4.64	33.40	16.0 ± 0.1	761	8.96	9.31	3.906
	10.1 ± 0.1	516	9.30	8.32	10.54	18.9 ± 0.1	802	10.5	11.3	7.619
	10.9 ± 0.2	589	13.5	16.1	19.26	25.9 ± 0.3	868	11.8	14.8	25.42
					34.42					10.691
323	9.1 ± 0.4	300	1.40	2.17	55.00					
	9.8 ± 0.2	364	5.46	3.85	29.49					
	10.1 ± 0.2	416	7.69	6.31	17.95					
	10.5 ± 0.1	472	10.2	10.7	4.902					
	11.4 ± 0.2	540	14.8	19.5	31.76					
					27.658					

Table 2. Solubility Constants *a*, *b*, and *C* Obtained from the Data Correlation Procedure

compound	a	b/K	C/m^3·kg^{-1}
Bpy	48.816	−14988.6	0.01008
DMBP	18.527	−6668.4	0.00883

with an uncertainty in pressure of ± 0.1 MPa over the range (0 to 35.0) MPa.

Solubility Measurement. A suitable amount of solute was charged into the high-pressure view cell, and the air in the cell was replaced by CO_2. The cell was then sealed. CO_2 was compressed carefully into the cell by a syringe pump at the controlled temperatures of (308, 313, 318, and 323) K. The fluid was stirred at a fixed pressure and the controlled temperature to obtain equilibrium. Stirring was paused for each observation. The pressure was increased gradually until the Bpy- or DMBP-rich phase disappeared completely and the system became a homogeneous transparent single phase. This pressure was defined as the dissolution pressure. The dissolution pressure and temperature were recorded to obtain the density of CO_2 in terms of IUPAC international thermodynamic tables.[8] The mole fraction, x, of the solute in the supercritical CO_2 was then calculated. This procedure was repeated at least three times at each condition. The uncertainty of the dissolution pressure and temperature was ± 0.5 MPa and ± 0.1 °C, respectively.[9,10] The mixtures were prepared gravimetrically.

Results and Discussion

The measured solubilities of Bpy and DMBP in supercritical CO_2 are listed in Table 1 as a function of solute mole fraction, pressure, and temperature and are also shown in Figure 1 as a function of mole fraction.

Each result listed in Table 1 is the average of at least three replicate measurement samples. The mole fractions of the solutes were reproducible to within ± 3 %. At a temperature, the solubilities of either compound in CO_2 increased with increasing pressure. At a given pressure, the solubilities of the compounds decreased with increasing temperature.

The results obtained in this study indicated that the solubility of Bpy (normal melting point temperature of 342 K) was higher than DMBP (normal melting point temperature of 447 K). The solubilities of Bpy and DMBP paralleled the order of their relative melting points. A similar behavior has been observed and reported in the literature.[11,12]

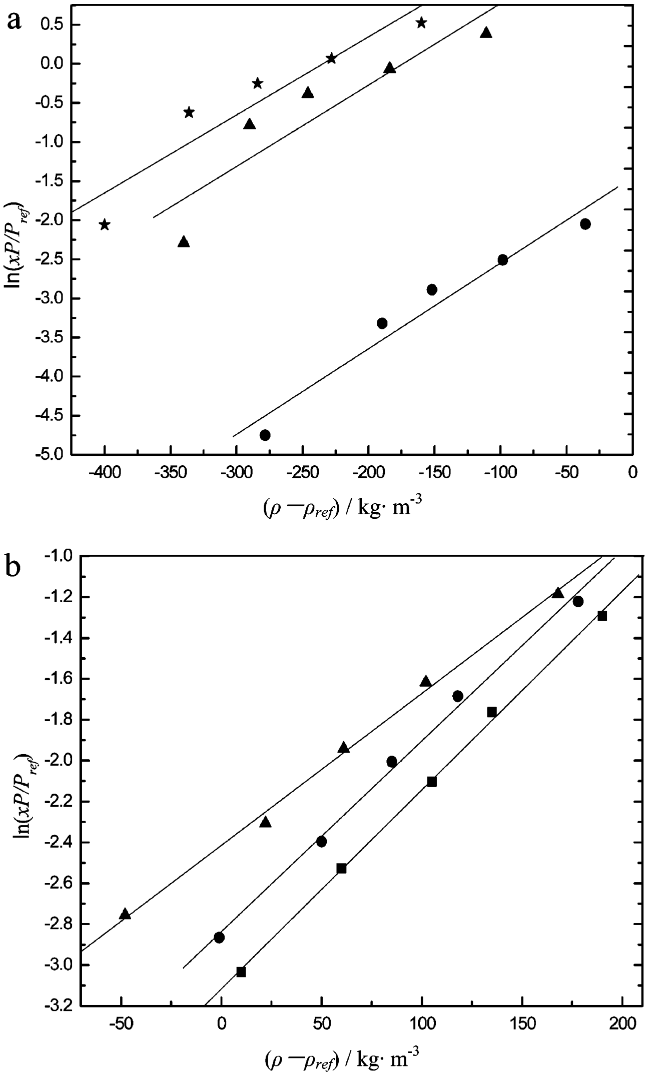

Figure 2. Plots of $\ln(xP/P_{ref})$ vs $(\rho - \rho_{ref})$/kg·m^{-3} for compounds at various temperatures: panel a, Bpy; panel b, DMBP. ■, 308 K; ●, 313 K; ▲, 318 K; ★, 323 K.

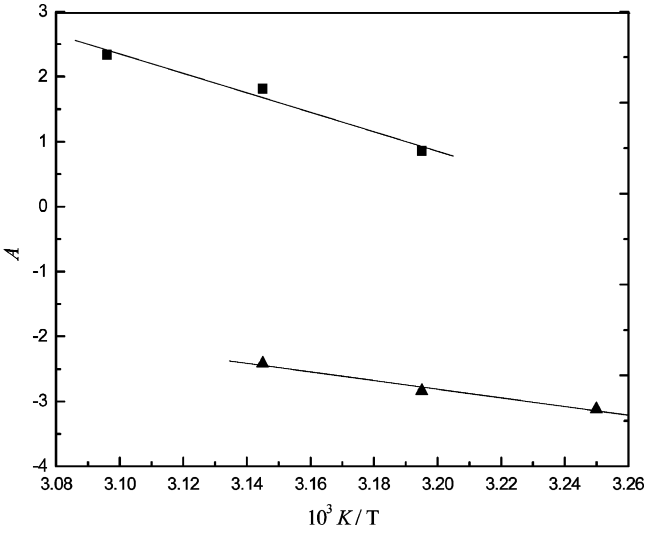

Figure 3. Plots of A vs $1/T$ for compounds. ■, Bpy; ▲, DMBP.

The experimental solubility data for the two compounds were fit to the following equation[13−16]

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

where

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

In eq 1, x is the mole fraction of the solutes; P is the pressure; $P_{\mathrm{ref}} = 0.1$ MPa; ρ is the density of pure CO_2 at the experimental temperature and pressure; $\rho_{\mathrm{ref}} = 700\ \mathrm{kg{\cdot}m^{-3}}$; and A, C, a, and b are adjustable parameters. The variation of $\ln(xP/P_{\mathrm{ref}})$ as a function of density, shown in Figure 2, was fit to eq 1 to obtain the A and C parameters. The values of C, obtained from the slopes of the corresponding plots, were then averaged for each compound and are listed in Table 2.

Using the average value of C, the experimental solubility data were then used to evaluate the A at each temperature for each compound. The variations of A with $1/T$ for each chelating agent are shown in Figure 3, and a and b were obtained by least-squares analysis. The resulting a and b values for compounds are also listed in Table 2. The values of a, b, and C were used to predict solubility using eq 1 and eq 2. The calculated data and the experimental data were compared, and the average absolute deviations (AARDs), listed in Table 1, were found to lie between (4.6 and 34.4) % and are, in view of the simplicity of the model and the uncertainty in the measured dissolution pressure of 0.5 MPa, not surprising.

Of most importance, however, is the observation that both Bpy and DMBP were of low solubility in supercritical CO_2, which is not favorable for metal ion extraction, and other mixtures, perhaps containing substituted Bpy or DMBP, might have a higher solubility in supercritical CO_2.

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