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Solubility of 1,5-Diaminobromo-4,8-dihydroxyanthraquinone in Supercritical Carbon Dioxide with or without Cosolvent[†]

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Dissolution of 1,5-diaminobromo-4,8-dihydroxyanthraquinone (C.I. Disperse Blue 56) in supercritical carbon dioxide was investigated at 393.15 K and 30 MPa over a wide range of contact times. Saturated solubility data of the disperse dyestuff in supercritical carbon dioxide with or without cosolvent were also measured at temperatures from (353.15 to 393.15) K and pressures up to 30 MPa. Either ethanol or dimethyl sulfoxide (DMSO) was used as a cosolvent. The experimental results showed that the equilibrium solubility can be effectively enhanced in the presence of both cosolvents. DMSO was found to yield higher solubility enhancement. The saturated solubility data were correlated with the Charstil and the Mendez-Santiago and Teja models. These two models correlated the solubility data to about within the experimental uncertainty.

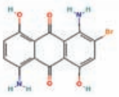
Introduction

The supercritical dyeing process has been proposed as a cleaner production method since the early 1990s.[1,2] Because supercritical fluids serve as good carriers for disperse dyestuffs in the dyeing process, dispersing agents and surfactants are unnecessary, and more importantly, excellent dyeing efficiency for both synthetic fabrics and natural fibers can be achieved.[1−5] This innovative dyeing method becomes a potential alternative to replace conventional dyeing methods, which have been recognized as high pollution and energy intensive processes. To develop the supercritical dyeing process, solubility data of disperse dyestuffs in supercritical fluids are of fundamental importance. Unfortunately, the related solubility data of disperse dyestuffs in supercritical carbon dioxide are still scarce in the literature.[6−27]

Supercritical carbon dioxide has limited solvent power for most polar and high molecular weight nonvolatile organic compounds due to its lack of polarity and incapability of specific interactions with solutes. As evidenced from experimental results,[28−36] the solubility of solutes in supercritical fluids can be greatly enhanced by adding a small amount of cosolvent, usually a polar or protic species such as acetone and ethanol. The solubility enhancement by the addition of cosolvent may be attributable to an increase of solvent density, modification of phase behavior, and augmentation of additional intermolecular interactions between cosolvent and solute molecules. Especially the presence of specific chemical intermolecular interactions between polar cosolvent and polar solute molecules such as hydrogen bonding and charge-transfer complex formation will lead to dramatic effects on both solubility enhancement and selectivity.[30−32,35]

In the present study, the solubility data of 1,5-diaminobromo-4,8-dihydroxyanthraquinone (C.I. Disperse Blue 56) in supercritical carbon dioxide with or without cosolvent were measured by using a semiflow type phase equilibrium apparatus over wide ranges of temperature and pressure. Ethanol and dimethyl sulfoxide (DMSO) were used as the cosolvents to explore the cosolvent effects on the solubility of the dyestuff in supercritical carbon dioxide. Ethanol is a preferable cosolvent because it is generally recognized as a safe compound. However, ethanol may form self-associating complexes in supercritical carbon dioxide.[37] DMSO, which has a high dipole moment, is a strong base and an excellent solvent for many disperse dyestuffs. Hydrogen bonding formation was expected between the cosolvents and 1,5-diaminobromo-4,8-dihydroxyanthraquinone molecules. The new solubility data were correlated with the Chrastil[38] and the Mendez-Santiago and Teja models[39] over the entire experimental conditions.

Table 1. Physical Properties of 1,5-Diaminobromo-4,8-dihydroxyanthraquinone (C.I. Disperse Blue 56)

formula	CAS number	MW	T_m/K	molecular structure	
$C_{14}H_9BrN_2O_4$	12217-79-7	349.14	453.4		
δ_2 /(cal·cm^{-3})$^{0.5}$	v_2^S /cm^3·mol^{-1}	T_b/K	$P_2^{sat\ d}$/MPa		
18.34[a]	201.03[b]	952.3[c]	353.15 K	373.15 K	393.15 K
			$1.28 \cdot 10^{-13}$	$2.34 \cdot 10^{-12}$	$3.09 \cdot 10^{-11}$

[a] Estimated from the Fedors method.[40] [b] Estimated from the Immirzi and Perini method.[41] [c] Taken from the ChemSpider Web site.[42] [d] Estimated from the Mackay method.[43]

Experimental Section

Materials. Carbon dioxide (99.5+ %) was supplied by Liu-Hsiang Gas Co. (Taiwan). Ethanol (99.5+ %) was purchased from Shimakyu Chemical (Japan) and DMSO (99.9+ %) from Arco Organics (USA). The dyestuff 1,5-diaminobromo-4,8-dihydroxyanthraquinone (C.I. Disperse Blue 56) (98+ %) was kindly provided from Continental Co. Ltd. (Taiwan). Some physical properties of the dyestuff are listed in Table 1, where T_m is the melting point determined from a differential scanning

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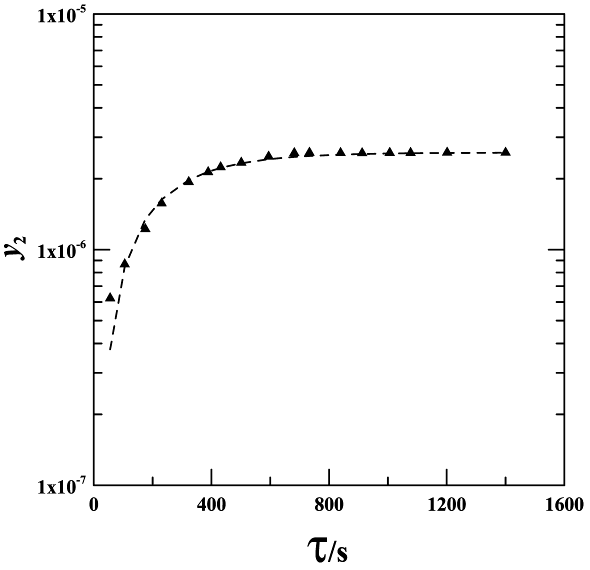

Figure 1. Concentration of 1,5-diaminobromo-4,8-dihydroxyanthraquinone (2) in supercritical carbon dioxide (1) over different lengths of contact time (τ) at 393.15 K and 30 MPa: ▲, experimental data; --, calculated results from eq 3.

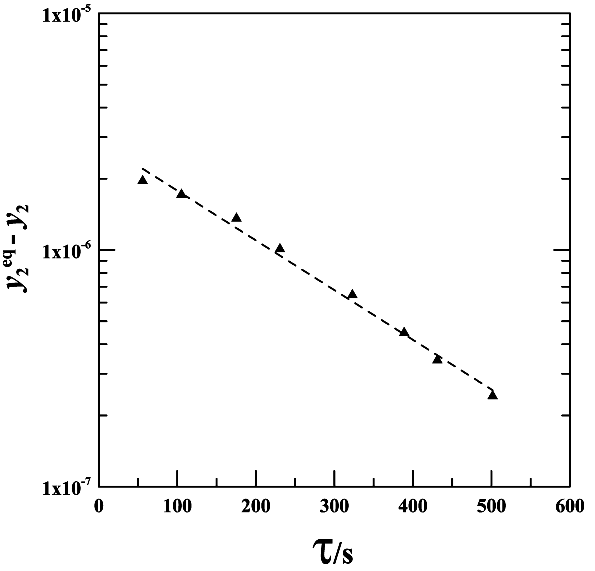

Figure 2. Variation of ($y_2^{\mathrm{eq}} - y_2$) with contact time (τ) for 1,5-diaminobromo-4,8-dihydroxyanthraquinone (2) in supercritical carbon dioxide (1): ▲, experimental data; --, calculated results from eq 3.

calorimeter (DSC) with an uncertainty of ± 0.5 K. The tabulated values of solubility parameter (δ), solid molar volume (v_2^{s}), normal boiling point (T_{b}), and sublimation pressures (P_2^{sat}) were estimated from the correlations as noted in the table. All the chemicals were used without further purification.

Equipment and Procedures. A semiflow type apparatus was employed in the present study to dissolve 1,5-diaminobromo-4,8-dihydroxyanthraquinone in supercritical carbon dioxide. The solid−gas equilibrium data were also measured with the same apparatus by running the dissolution experiments under sufficiently long contact time. The schematic diagram of the apparatus and the experimental procedure have been given elsewhere.[27] The uncertainty of the measured variables is ± 0.1 mg for mass, ± 0.02 K for temperature, ± 0.1 % for pressure, and ± 0.25 % for total volume of carbon dioxide.

Composition Analysis. The concentration of the dyestuff in the collected samples was analyzed with an UV/visible spectrophotometer. The wavelength of the light source was set to 640 nm. Calibration was made with at least six standard samples over the dye mass fraction range of $0.05 \cdot 10^{-6}$ to $20 \cdot 10^{-6}$. A linear equation was applied to correlate the concentrations with absorbencies. In general, the uncertainty of the solubility measurements was estimated to be about ± 10 %.

Table 2. Solubilities of 1,5-Diaminobromo-4,8-dihydroxyanthraquinone in Supercritical Carbon Dioxide

T/K	P/MPa	$10^7 \cdot y_2$	$\rho_{\mathrm{CO2}}{}^{a}$/g·dm^{-3}
353.15	15.00	0.39	427.15
	20.00	2.60	593.89
	25.00	5.87	686.22
	30.00	10.4	745.60
373.15	15.00	0.33	332.35
	20.00	2.52	480.53
	25.00	7.31	588.45
	30.00	16.9	661.87
393.15	15.00	0.35	280.36
	20.00	3.45	401.15
	25.00	9.51	505.56
	30.00	25.8	585.22

[a] Taken from NIST Chemistry WebBook.[44]

Results and Discussion

Dissolution of Dyes at Different Lengths of Contact Time. The mole fraction of the dyestuff in supercritical carbon dioxide was measured at 393.15 K and 30 MPa over a wide range of contact times. Figure 1 illustrates the variations of dye concentration in mole fraction (y_2) with contact time (τ) for 1,5-diaminobromo-4,8-dihydroxyanthraquinone. The definition of contact time is given by

$$\tau = m_2/\dot{m}_1 \tag{1}$$

where m_2 refers to the mass of dye packed in the dissolution cell and $\dot{m}_1$ represents the mass flow rate of carbon dioxide. It shows that an equilibrium state was attained when the lengths of the contact time are longer than 600 s.

Under the diffusion-controlled assumption, the dissolution rate of solid dyestuff in supercritical carbon dioxide can be expressed by the following equation

$$\mathrm{d}y_2/\mathrm{d}\tau = k_{\mathrm{o}}(y_2^{\mathrm{eq}} - y_2) \tag{2}$$

where y_2^{eq} is the equilibrium mole fraction and k_{o} is an effective mass transfer coefficient. Integration of eq 2 yields

$$\ln(y_2^{\mathrm{eq}} - y_2) = k_{\mathrm{o}}\tau + k_1 \tag{3}$$

where k_1 is an integration constant. If the diffusion-controlled assumption is valid, the values of $\ln(y_2^{\mathrm{eq}} - y_2)$ should vary linearly with contact time. Figure 2 illustrates that the linear relation is obeyed when the lengths of contact time are shorter than 500 s. The effective mass transfer coefficient ($k_{\mathrm{o}} = 0.00483$ s^{-1}) was determined by fitting the experimental values to eq 3.

Equilibrium Solubility. During the measurements of equilibrium solubility, the contact time was kept at approximately 1200 s to ensure the attainment of equilibrium states in the gas phase. The equilibrium solubilities of 1,5-diaminobromo-4,8-dihydroxyanthraquinone in carbon dioxide were measured at temperatures from (353.15 to 393.15) K over a pressure range of (15 to 30) MPa. Table 2 lists the experimental results together with the density of pure carbon dioxide[44] at each operating condition. Over the entire experimental conditions, the mole fractions of the dyestuff are in the range of 10^{-8} to 10^{-6}. Since carbon dioxide is nonpolar, the solid−gas equilibrium behavior

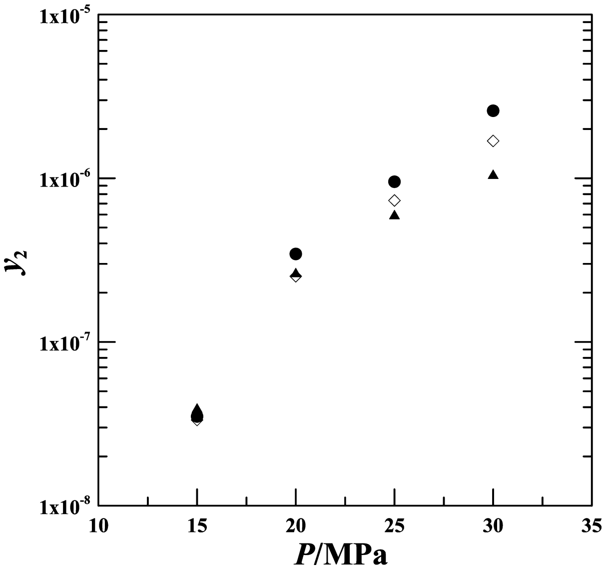

Figure 3. Equilibrium solubilities (y_2) of 1,5-diaminobromo-4,8-dihydroxyanthraquinone (2) in supercritical carbon dioxide (1): ▲, 353.15 K; ◇, 373.15 K; ●, 393.15 K.

may be governed mainly by the physical interactions between carbon dioxide and the dye molecules. No specific interactions were expected in this binary system, and thus the solubility of 1,5-diaminobromo-4,8-dihydroxyanthraquinone in supercritical CO_2 is rather low. Figure 3 shows the equilibrium solubility of 1,5-diaminobromo-4,8-dihydroxyanthraquinone varying with pressure at (353.15, 373.15, and 393.15) K, indicating that the solubility increases with increasing pressure. While the saturated solubility of 1,5-diaminobromo-4,8-dihydroxyanthraquinone increases about 27-fold as pressure increases from (15 to 30) MPa at 353.15 K, the solubility increases about 74-fold at 393.15 K under the same pressure increment.

The solubility isotherms have a crossover at pressures around (15 to 20) MPa as shown in Figure 3. Below the crossover pressure, the solubility decreases with increasing temperature, whereas an opposite trend was exhibited at pressures higher than the crossover pressure. The crossover phenomena could be attributed to the competitions between solute's vapor pressure and solvent's density, whose temperature dependences are in opposite directions. At the crossover point, these two competitive factors are even. Several investigators have already found the existence of retrograde vaporization in binary solid−supercritical fluid systems.[20,35] The significance of crossover phenomena has been discussed in detail by Foster et al.[45]

Table 3. Solubilities of 1,5-Diaminobromo-4,8-dihydroxyanthraquinone (y_2) in Supercritical CO_2 with Mole Fraction y_3 of Cosolvent Ethanol

		353.15 K	393.15 K
P/MPa	y_3	$10^7 \cdot y_2$	$10^7 \cdot y_2$
15.00	0.0100	0.45	–
	0.0300	0.58	–
	0.0500	0.80	–
20.00	0.0100	2.67	3.84
	0.0300	3.50	4.39
	0.0500	4.75	5.30
25.00	0.0100	6.08	10.3
	0.0300	7.77	12.5
	0.0500	10.6	15.0
30.00	0.0100	11.3	27.2
	0.0300	13.7	30.7
	0.0500	18.8	34.5

Table 4. Solubilities of 1,5-Diaminobromo-4,8-dihydroxyanthraquinone (y_2) in Supercritical CO_2 with Mole Fraction y_3 of Cosolvent DMSO at 353.15 K

P/MPa	y_3	$10^6 \cdot y_2$
20.00	0.0100	0.43
	0.0300	0.65
	0.0500	0.91
25.00	0.0100	1.10
	0.0300	1.50
	0.0500	2.44
30.00	0.0100	2.04
	0.0300	2.95
	0.0500	4.28

Table 5. Correlated Results from the Chrastil Equation

mixture	*k*	*a*	*b*	100 · ARD C^a
CO_2 + dye^b	6.71	−8112.65	−26.61	6.4
cosolvent: ethanol (3)				
CO_2 + dye^b + (y_3 = 0.0100)	6.54	−8095.22	−25.45	7.9
CO_2 + dye^b + (y_3 = 0.0300)	6.47	−7737.14	−25.79	5.7
CO_2 + dye^b + (y_3 = 0.0500)	6.40	−7156.76	−26.70	6.3
cosolvent: DMSO (3)				
CO_2 + dye^b + (y_3 = 0.0100)	7.81	−56.10^c	–	2.2
CO_2 + dye^b + (y_3 = 0.0300)	7.53	−53.94^c	–	5.6
CO_2 + dye^b + (y_3 = 0.0500)	7.80	−55.27^c	–	0.1

[a] ARD $C = (1/N)\sum_{i=1}^{N} |C_i^{\text{calcd}} - C_i^{\text{exptl}}|/C_i^{\text{exptl}}$, where C is the concentration of dye in the saturated gas phase and N is the number of data points. [b] 1,5-Diaminobromo-4,8-dihydroxyanthraquinone (C.I. Disperse Blue 56). [c] The value of $a' = (a/353.15) + b$.

Cosolvent Effects on the Solubilities of Disperse Dye. The solvent mixtures of cosolvent and carbon dioxide should form a homogeneous phase during the solubility measurements. The solvent mixtures exist as a supercritical homogeneous phase if the operating pressures are higher than the critical value at the equilibrium temperature, regardless of the compositions of the solvent mixtures. Galicia-Luna and Ortega-Rodriguez[46] reported that the critical pressure is about 12.46 MPa at 348.40 K for the carbon dioxide + ethanol binary system. With the aid of the phase equilibria (PE) package,[47] the critical pressure of ethanol + carbon dioxide at 393.15 K was estimated to be about 17 MPa from the Soave equation of state.[48] As a consequence, the equilibrium measurements in the presence of cosolvent ethanol at (353.15 and 393.15) K were conducted at pressures ranging from (15 to 30) MPa and (20 to 30) MPa, respectively. For the DMSO cosolvent system at 353.15 K, the operating pressures were selected in a range of (20 to 30) MPa. Over these operating conditions, the solvent mixtures of carbon dioxide plus DMSO are very likely to form a homogeneous supercritical phase.[49] In these series of runs, the contact time was manipulated at approximately 1400 s, which is sufficiently long to attain equilibrium states for the gas-phase samples. Tables 3 and 4 list the saturated solubility data in the presence of cosolvent ethanol and DMSO, respectively. It indicates that the addition of the cosolvents can markedly enhance the solubility of 1,5-diaminobromo-4,8-dihydroxyanthraquinone in supercritical solvent mixtures, and the solubility enhancement increases with an increase of cosolvent concentration.

At the same operating condition, the enhancement induced by the DMSO is obviously greater than that by ethanol. The comparison of cosolvent effects resulting from DMSO and ethanol can be qualitatively interpreted on the basis of intermolecular interactions. Intermolecular interactions between the dye and cosolvent molecules may involve physical forces and specific chemical forces. The physical interactions between polar 1,5-diaminobromo-4,8-dihydroxyanthraquinone molecules and the polar cosolvent molecules of ethanol or DMSO should include electrostatic, induction, and dispersion forces. According

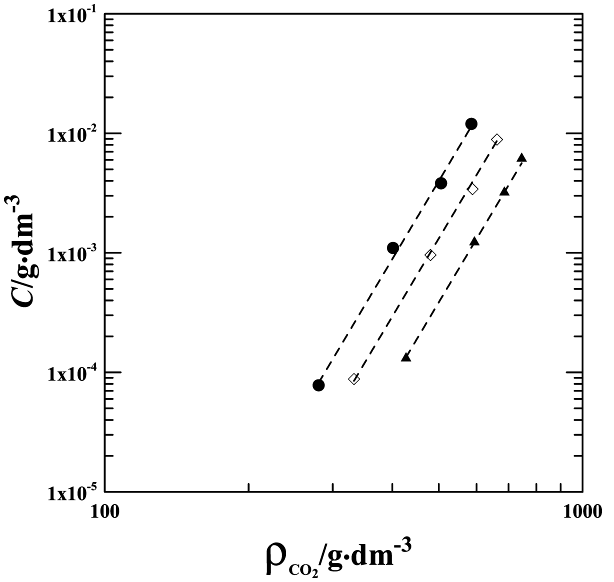

Figure 4. Comparison of the correlated results from the Chrastil equation with experimental values for the CO_2 (1) + 1,5-diaminobromo-4,8-dihydroxy- anthraquinone (2): ▲, 353.15 K; ◇, 373.15 K; ●, 393.15 K; --, calculated results with the Chrastil equation.

to the molecular structure as shown in Table 1, 1,5-diaminobromo-4,8-dihydroxyanthraquinone contains four hydrogen-bond donor sites and six hydrogen-bond acceptor sites. Ethanol is a protic solvent that can donate a proton. DMSO is a strong hydrogen-bond acceptor due to its sulfinyl group (SO).[50] Specific hydrogen bonds are expected to be formed between the carbonyl group of 1,5-diaminobromo-4,8-dihydroxyanthraquinone and the hydroxyl group of ethanol and also between the N−H group of the dyestuff and the SO group of DMSO. The strong tendency of the DMSO oxygen to act as a hydrogen-bond acceptor may lead to complex formation of the dyestuff with DMSO molecules. Although ethanol molecules are able to form hydrogen bonds with 1,5-diaminobromo-4,8-dihydroxyanthraquinone, self-association may also occur simultaneously[37] and thus leads to reducing the cosolvent effect of ethanol on the enhancement of the dye solubility. Moreover, the dipole moment of DMSO ($1.4 \cdot 10^{-29}$ C·m) is much greater than that of ethanol ($5.7 \cdot 10^{-30}$ C·m). It implies that the physical forces of the DMSO/1,5-diaminobromo-4,8-dihydroxyanthraquinone pair are also much stronger than those of the ethanol/1,5-diaminobromo-4,8-dihydroxyanthraquinone pair. Therefore, the solubility enhancements resulting from the presence of the DMSO cosolvent are obviously higher than those from ethanol.

Data Correlation. The Chrastil model[38] was used in the present study for correlating the equilibrium solubility data. This model was developed on the basis of the complex formation of solute with supercritical solvent in the gas phase and widely used to correlate the equilibrium solubility data. The model was defined as

$$\ln(C/\mathrm{g \cdot dm^{-3}}) = k \ln(\rho/\mathrm{g \cdot dm^{-3}}) + a/(T/\mathrm{K}) + b \quad (4)$$

where C is the concentration of solid compound in the saturated gas phase; k is the number of solvent molecules associating with one molecule of solute to form a solvated complex; ρ is the density of supercritical fluid; T is equilibrium temperature; and a and b are constants. Because the concentrations of solute and cosolvent in the gas phase are relatively dilute, the densities of supercritical fluid mixtures can be reasonably assumed as the same values of pure carbon dioxide, which were taken from the NIST Chemistry WebBook.[44] As defined in eq 4, the Chrastil equation is linear on a log−log graph of the solid concentration C versus density ρ. Table 5 lists the correlated results, and Figure 4 presents the comparison of the calculated results with the experimental values for 1,5-diaminobromo-4,8-dihydroxyanthraquinone in supercritical carbon dioxide. The Chrastil equation correlated the equilibrium solubility data of 1,5-diaminobromo-4,8-dihydroxyanthraquinone to within experimental uncertainty. As also shown in Table 5, the value of association number k is about 7 for the system without cosolvent. The values of k slightly decrease in the case of using ethanol as a cosolvent, while those of k slightly increase up to about 8 in the presence of DMSO as the cosolvent.

The solubility data were also correlated with a semiempirical model of Mendez-Santiago and Teja,[39] which was derived by using a classical expansion of the Helmholtz energy around the critical point of solvent to represent the mixture properties at infinite dilution. The correlated results from the Mendez-Santiago and Teja model are generally comparable with those from the Chrastil equation, except for the CO_2 + 1,5-diaminobromo-4,8-dihydroxyanthraquinone.

Conclusions

The dissolution of 1,5-diaminobromo-4,8-dihydroxyanthraquinone (C.I. Disperse Blue 56) in supercritical carbon dioxide has been investigated with a semiflow apparatus over a wide range of contact times. A diffusion-controlled model represented well the experimental results, and the effective mass-transfer coefficient was determined by fitting the dissolution data to this simple mass-transfer model. The saturated solubilities of 1,5-diaminobromo-4,8-dihydroxyanthraquinone in supercritical carbon dioxide with or without cosolvents have also been measured in a temperature range of (353.15 to 393.15) K and pressures up to 30 MPa. The isothermal solubilities of 1,5-diaminobromo-4,8-dihydroxyanthraquinone in supercritical CO_2 increased with increasing pressure, and crossover behavior was also found in the CO_2 + 1,5-diaminobromo-4,8-dihydroxyanthraquinone binary system. Either protic ethanol or aprotic DMSO has been used as a cosolvent to enhance dye's solubility. Both cosolvents effectively increased the solubility of 1,5-diaminobromo-4,8-dihydroxyanthraquinone, but DMSO induced higher solubility enhancement than ethanol. In general, the Chrastil equation correlated the solubility data to about within the experimental uncertainty. The calculated results from the Mendez-Santiago and Teja model showed that the solubility data were consistent over the entire experiment conditions.

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