Solubility of C.I. Disperse Violet 1 in Supercritical Carbon Dioxide with or without Cosolvent

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Dissolution of C.I. Disperse Violet 1 with supercritical carbon dioxide was investigated at 393.2 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 (353.2 to 393.2) K and pressures up to 30 MPa. Either ethanol or dimethyl sulfoxide (DMSO) was used as a cosolvent. As evidenced from the experimental results, the equilibrium solubility can be effectively enhanced in the presence of both cosolvents. DMSO was found to yield greater solubility enhancement. The saturated solubility data were correlated with the Charstil and the Mendez–Santiago and Teja models. The Chrastil model correlated the solubility data to about within the experimental uncertainty. The correlated results from the Mendez–Santiago–Teja model showed that the solubility data were consistent.

Introduction

The supercritical dyeing process has been recognized as an environmental friendly technology. This innovative method could be one potential alternative to replace the conventional high-polluting and energy-consuming dyeing processes. Both synthetic fabrics and natural fibers can be dyed in supercritical carbon dioxide, which is used as a carrier of disperse dyestuffs without adding any dispersing agents and surfactants. Excellent dyeing efficiency can be achieved from this dyeing method.^{1–7} To develop the supercritical dyeing processes, solubility data of disperse dyestuffs in supercritical fluids are fundamentally important. Unfortunately, the related solubility data of disperse dyestuffs in supercritical carbon dioxide are still scarce in the literature.^{8–28}

Supercritical carbon dioxide has limited solvent power for most polar and high molecular weight, nonvolatile organic substances due to the lack of polarity and incapability to participate in the specific interactions with solutes. As evidenced from experimental results,^{29–49} the solubility of solutes in supercritical fluids can be greatly enhanced by addition of a small amount of cosolvent, usually a polar or protic species such as acetone and ethanol. The solubility enhancement by adding cosolvent may be attributable to an increase of solvent density, modification of phase behavior, and generation of additional intermolecular interactions between cosolvent and solute molecules. The presence of cosolvent generally increases the molar density of solvent mixtures and thus improves the solvent power.^{50–53} The increase of density is pronounced near the critical point of the solvent mixture, in which the isothermal compressibility is large. However, the cosolvent effects become insignificant in the dense supercritical region.³⁴ The reduction of the upper critical end pressure is a means to modify the phase behavior by introducing cosolvents. This can allow the processes to be operated at easier accessible pressures with sufficiently high solvent power.54,55

* Corresponding author. Tel.: +886-2-2737-6626. Fax: +886-2-2737-6644. E-mail: mjlee@mail.ntust.edu.tw. The phase behavior of mixtures is governed by the physical forces and the chemical forces among the constituent molecules. Especially, the existence of chemical forces such as hydrogen bonding and charge-transfer complex formation between the polar cosolvent and the polar solute will lead to dramatic effects on both solubility enhancement and selectivity.^{36,56} Several investigators^{34,43,57} have observed such substantial solubility enhancement and/or selectivity improvement due to hydrogen bonding formation. A case of charge-transfer complex formation between solute and cosolvent molecules was also reported by Ekart et al.³⁷

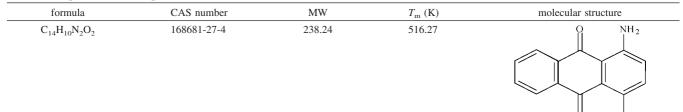
In the present study, the solubility data of C.I. Disperse Violet 1 in supercritical carbon dioxide with or without cosolvent were measured by using a semiflow type phase equilibrium apparatus in wide ranges of temperature and pressure. Ethanol and dimethyl sulfoxide (DMSO) were individually adopted as a cosolvent 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 substance. However, ethanol molecules may form self-associating complexes in supercritical carbon dioxide.58 DMSO, which has high dipole moment, is a strong base and an excellent solvent for many disperse dyestuffs. Hydrogen bonding formation was expected between the cosolvents and C.I. Disperse Violet 1 molecules. The new solubility data were correlated with the Chrastil equation⁵⁹ and the Mendez-Santiago and Teja model⁶⁰ over the entire experimental conditions.

Experimental Section

Materials. Carbon dioxide (99.8+ %) 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 C.I. Disperse Violet 1 (97+ %) was kindly provided from Continental Co. Ltd. (Taiwan). Some basic information of the dyestuff is given in Table 1, where $T_{\rm m}$ is the melting point measured with a differential scanning calorimeter (DSC). All the chemicals were used without further purification.

Equipment and Procedures. A semiflow type apparatus was employed in the present study to extract C.I. Disperse Violet 1

Table 1. Properties of C.I. Disperse Viole	et	L
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with supercritical carbon dioxide. The solid-gas equilibrium data were also measured with the same apparatus by running the extraction experiments under sufficiently long contact time. The schematic diagram of the extraction apparatus and the experimental procedures have been presented in our previous study.²⁸ In this section, a brief description for the sampling method is given as follows. The gas stream leaving the extractor was expanded to atmospheric pressure through a heated needle

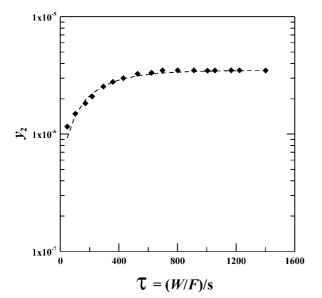


Figure 1. Concentration of C.I. Disperse Violet 1 in supercritical carbon dioxide over different lengths of contact time (τ) at 393.2 K and 30 MPa: \blacklozenge , experimental data; --, calculated results from eq 3.

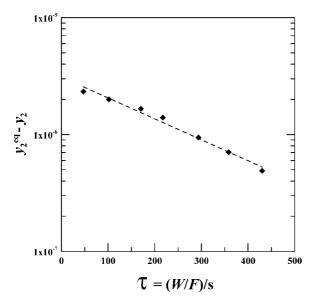


Figure 2. Variation of $(y_2^{\text{eq}} - y_2)$ with contact time (τ) for C.I. Disperse Violet 1 in supercritical carbon dioxide: \blacklozenge , experimental data; --, calculated results from eq 3.

valve and a heated micrometering valve. The expanded mixture was diverted into a sampling train, which was composed of two test tubes in series. The test tubes were filled with DMSO to dissolve the extracted dyestuff, and glass beads were also placed in the test tubes to promote the contact of sampling stream with DMSO. A solvent reservoir, connected in between the needle valve and the micrometering valve, was used for removal of dyestuff left in the expansion zone at the end of each run. The spent solution was also collected in the sampling tubes. The concentration of dyestuff in the collected solution was determined by an UV/visible spectrophotometer (U-1500, Hitachi, Japan).

ŃΗ₂

During the equilibrium measurements, the mass flow rate of carbon dioxide was regulated at about 0.0016 $g \cdot s^{-1}$, and the amount of packed dyestuff in the equilibrium cells was about 2 g. Under these circumstances, the flow rate was found sufficiently slow to ensure that solvent mixtures can be saturated with the dyestuff before leaving the extractor. The attainment

 Table 2.
 Solubilities of C.I. Disperse Violet 1 in Supercritical Carbon Dioxide

<i>T</i> /K	<i>P</i> /MPa	$10^7 \cdot y_2$	$C/g \cdot dm^{-3}$	$\rho_{\rm CO_2}{}^a/{\rm g}\cdot{\rm dm}^{-3}$
353.2	15	1.36	0.00031	427.15
	20	7.48	0.00240	593.89
	25	15.3	0.00569	686.22
	30	27.7	0.01119	745.60
373.2	15	0.73	0.00013	332.35
	20	5.60	0.00146	480.53
	25	13.7	0.00436	588.45
	30	32.7	0.01173	661.87
393.2	15	0.53	0.00008	280.36
	20	3.82	0.00083	401.15
	25	11.7	0.00319	505.56
	30	34.9	0.01105	585.22

^a Taken from NIST Chemistry WebBook.⁶¹

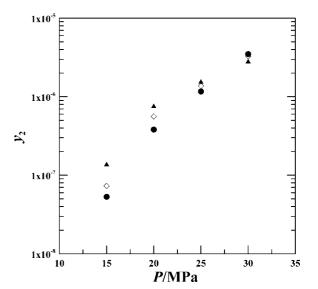


Figure 3. Equilibrium solubilities (y_2) of C.I. Disperse Violet 1 in supercritical carbon dioxide: \blacktriangle , 353.2 K; \diamondsuit , 373.2 K; \blacklozenge , 393.2 K.

Table 3.	Solubilities of C.I. Disperse Violet 1 (y ₂) in Supercritical
CO ₂ with	1 Mole Fraction y ₃ of Cosolvent Ethanol

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		T = 353.2 K	T = 393.2 K
P/MPa	<i>y</i> ₃	$10^7 \cdot y_2$	$10^7 \cdot y_2$
15	0.01	1.74	_
	0.03	2.21	-
	0.05	2.72	-
20	0.01	8.72	5.08
	0.03	10.7	6.15
	0.05	12.9	8.38
25	0.01	16.4	14.5
	0.03	20.3	18.0
	0.05	24.8	22.1
30	0.01	28.7	39.8
	0.03	34.9	51.0
	0.05	40.9	58.5

Table 4. Solubilities of C.I. Disperse Violet 1 (y_2) in Supercritical CO₂ with Mole Fraction y_3 of Cosolvent DMSO at 353.2 K

P/MPa	<i>y</i> ₃	$10^{6} \cdot y_2$
20	0.01	1.98
	0.03	3.56
	0.05	6.29
25	0.01	3.79
	0.03	5.50
	0.05	8.59
30	0.01	6.04
	0.03	7.98
	0.05	10.6

Table 5. Cosolvent-Enhancement Parameters (Ψ) for the Investigated Systems

<i>P</i> /MPa	Ψ (at $y_3 = 0.01$)	Ψ (at $y_3 = 0.03$)	Ψ (at $y_3 = 0.05$)
	Cosolvent: et	hanol (3), $T = 353.2$	K
15	1.28	1.63	2.01
20	1.17	1.44	1.72
25	1.07	1.33	1.62
30	1.04	1.26	1.48
	Cosolvent: et	hanol (3), $T = 393.2$	К
20	1.33	1.61	2.20
25	1.25	1.54	1.89
30	1.14	1.46	1.68
	Cosolvent: D	MSO (3), $T = 353.2$	K
20	2.65	4.76	8.42
25	2.48	3.60	5.61
30	2.18	2.88	3.82

of equilibrium has been verified by measuring the concentrations of dyestuff in carbon dioxide at different lengths of contact time. At least four replicates were taken at each experimental condition. The solubility was obtained by averaging these replications. Generally, the uncertainty of the solubility measurements was estimated to be about \pm 10 %, while the uncertainties of temperature and pressure measurements were within \pm 0.1 K and \pm 0.1 %, respectively.

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 597 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.

Results and Discussion

Extraction of Dyes at Different Lengths of Contact Time. The mole fraction of the dyestuff in supercritical carbon dioxide was measured at 393.2 K and 30 MPa over a wide range of contact times. Figure 1 illustrates the variations of dye mole

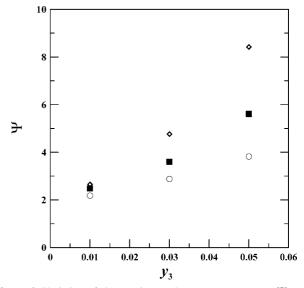


Figure 4. Variation of the cosolvent-enhancement parameter (Ψ) with cosolvent mole fraction (y_3) for C.I. Disperse Violet 1 in supercritical carbon dioxide with cosolvent DMSO at 353.2 K: \diamond , P = 20 MPa; \blacksquare , P = 25 MPa; \bigcirc , P = 30 MPa.

fraction (y_2) with contact time (τ) for C.I. Disperse Violet 1. The definition of contact time is given by

$$\tau = W/F \tag{1}$$

where W refers to the mass of dye packed in the extractors and F represents the mass flow rate of carbon dioxide. It shows that the equilibrium state was attained when the length of the contact time was greater than 700 s.

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

$$dy_2/d\tau = k_0(y_2^{eq} - y_2)$$
(2)

where y_2^{eq} is the equilibrium mole fraction and k_0 is an effective mass transfer coefficient. Integration of eq 2 yields

$$\ln(y_2^{eq} - y_2) = -k_0 \tau + k_1 \tag{3}$$

where k_1 is an integration constant. If the diffusion-controlled assumption is valid, the values of $\ln(y_2^{eq} - y_2)$ would 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 ($k_0 = 0.00412$ 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 saturation of dye in the gas phase samples. The equilibrium solubilities of C.I. Disperse Violet 1 in carbon dioxide were measured at temperatures from (353.2 to 393.2) K over a pressure range of (15 to 30) MPa. Table 2 lists the experimental results together with the density of pure carbon dioxide⁶¹ 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 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 C.I. Disperse Violet 1 in supercritical CO₂ is rather low. Figure 3 shows the equilibrium solubility of C.I. Disperse Violet 1 varying with pressure at (353.2, 373.2, and 393.2) K. The isothermal solubilities of C.I.

Table 6. Correlated Results from the Chrastil Equation

mixture	k	a	b	AARD C^{a} (%)
mixtuit	ĸ	a	U	AARD C (%)
$CO_2 + C.I.$ Disperse Violet 1	6.44	-4993.82	-32.96	7.6
	Cosolvent:	ethanol (3)		
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.01$	6.06	-5051.73	-30.26	6.8
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.03$	6.05	-5053.96	-29.97	7.8
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.05$	5.87	-5037.30	-28.72	6.2
	cosolvent:	DMSO (3)		
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.01$	5.85	-42.45^{b}	_	2.6
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.03$	4.49	-33.18^{b}	_	3.4
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.05$	3.27	-24.80^{b}	_	0.8
2 1 73			-	

^{*a*} AARD $C(\%) = (100 \%/N)\sum_{i=1}^{N} |C_i^{\text{alcd}} - C_i^{\text{expl}}|/C_i^{\text{expl}}|$, where C is the concentration of dye in the saturated gas phase and N is the number of data points. ^{*b*} The value of a' = (a/353.2) + b.

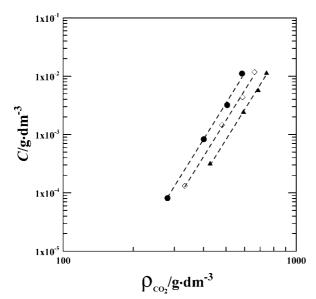


Figure 5. Comparison of the correlated results from the Chrastil equation with experimental values for the CO_2 (1) + C.I. Disperse Violet 1 (2) system: \blacktriangle , 353.2 K; \diamondsuit , 373.2 K; \blacklozenge , 393.2 K; --, calculated results with the Chrastil equation.

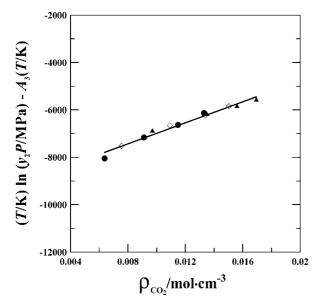


Figure 6. Comparison of the correlated results from the Mendez–Santiago and Teja model with experimental values for the CO_2 (1) + C.I. Disperse Violet 1 (2) system: \blacktriangle , 353.2 K; \diamondsuit , 373.2 K; \diamondsuit , 393.2 K; -, calculated results with the Mendez–Santiago & Teja model.

Disperse Violet 1 increase with increasing pressure. While the saturated solubility of C.I. Disperse Violet 1 increases about 20-fold as pressure increases from (15 to 30) MPa at 353.2 K,

the solubility increases about 66-fold at 393.2 K under the same pressure increment.

The solubility isotherms have a crossover at pressures around (25 to 30) 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.^{22,43,56,62,63} The significance of crossover phenomena has been discussed in detail by Foster et al.⁶³

Cosolvent Effects on the Solubilities of Disperse Dye. To study the cosolvent effects, 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 extraction pressures are higher than the critical value at the corresponding extraction temperature, regardless of the compositions of the solvent mixtures. Galicia-Luna et al.⁶⁴ 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) program,⁶⁵ the critical pressure of ethanol + carbon dioxide at 393.2 K was estimated to be about 17 MPa from the Soave equation of state.⁶⁶ As a consequence, the equilibrium measurements in the presence of cosolvent ethanol at (353.2 and 393.2) K were conducted at pressures ranging from (15 to 30) MPa and from (20 to 30) MPa, respectively. For the DMSO cosolvent system, the operating pressures were selected in a range of (20 to 30) MPa as the equilibrium temperature was 353.2 K. Over these operating conditions, the solvent mixtures of carbon dioxide plus DMSO may form a homogeneous supercritical phase.⁶⁷ In these series of runs, the contact time was set at approximately 1400 s, which is sufficiently long to attain equilibrium states for the gas-phase samples. Tables 3 and 4 report the saturated solubility data in the presence of cosolvent ethanol and DMSO, respectively. It is indicated that the addition of the cosolvents can markedly enhance the solubility of C.I. Disperse Violet 1 in supercritical solvent mixtures.

To conveniently express the solubility enhancement induced by cosolvent, a cosolvent-enhancement parameter, Ψ , is defined as follows.

$$\Psi(P, T, y_3) = y_2(P, T, y_3) / y_2(P, T, y_3 = 0)$$
(4)

where $y_2(P, T, y_3)$ refers to the dyestuff's equilibrium solubility at *T* and *P* containing a cosolvent mole fraction equal to y_3 and $y_2(P, T, y_3 = 0)$ is the equilibrium solubility in the absence of cosolvent at the same temperature and pressure. The value of

Table 7. Correlated Results from the Mendez-Santiago and Teja Model

mixture	A_1	A_2	A_3	AARD y_2^a (%)
$CO_2 + C.I.$ Disperse Violet 1	-9203.42	221712	6.43	25.0
	Cosolvent: ethan	ol (3)		
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.01$	-8760.27	182639	6.78	15.0
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.03$	-8769.43	182393	7.03	16.3
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.05$	-8681.12	177321	7.17	13.3
	Cosolvent: DMS	O (3)		
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.01$	-5676.77^{b}	155036	_	2.3
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.03$	-5040.74^{b}	123077	_	3.5
$CO_2 + C.I.$ Disperse Violet $1 + y_3 = 0.05$	-4450.61^{b}	94581	_	1.3

^{*a*} AARD $y_2(\%) = (100 \ \%/N) \sum_{i=1}^{N} |y_{2,i}^{calcd} - y_{2,i}^{expl}|/y_{2,i}^{expl}|$, where N is the number of data points and y_2 is the mole fraction of the dye in the saturated gas phase. ^{*b*} The value of $A'_1 = A_1 + A_3 \cdot 353.2$.

the cosolvent-enhancement parameter, Ψ , depends on temperature, pressure, cosolvent concentration, and the nature of cosolvent. Table 5 lists the cosolvent-enhancement parameters with cosolvent ethanol or DMSO. As seen from the tabulated values, the cosolvent-enhancement parameter increases with an increase of either temperature or cosolvent concentration but decreases with increasing pressure. Figure 4 graphically illustrates the effect of cosolvent concentration of DMSO on the cosolvent-enhancement parameter.

At the same operating condition, the enhancement induced by 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 C.I. Disperse Violet 1 molecules and the polar cosolvent molecules of ethanol or DMSO should include electrostatic, induction, and dispersion forces. According to the molecular structure, C.I. Disperse Violet 1 contains two hydrogen bond donor sites and four hydrogen bond acceptor sites. Ethanol is a protic solvent that can donate hydrogen bonds. DMSO is a strong hydrogen-bond acceptor due to its sulfinyl group (S=O).⁶⁸ Specific hydrogen bondings are expected to be formed between the carbonyl group of C.I. Disperse Violet 1 and the hydroxyl group of ethanol, and also between the N-H group of the dyestuff and the S=O group of DMSO. The strong tendency of the DMSO oxygen to act as a hydrogen-bond acceptor may lead to a number of complexes of the dyestuff with DMSO molecules. Although ethanol molecules are able to form hydrogen bonds with C.I. Disperse Violet 1 (amphiprotic molecules), self-association may occur simultaneously and thus leads to reducing the cosolvent effect of ethanol on the enhancement of the dye solubility. Moreover, the dipole moment of DMSO $(1.4 \cdot 10^{-29} \text{ C} \cdot \text{m})$ is much greater than that of ethanol $(5.7 \cdot 10^{-30} \text{ C} \cdot \text{m})$. It implies that the physical forces of the DMSO + C.I. Disperse Violet 1 pair are also much stronger than those of the ethanol + C.I. Disperse Violet 1 pair. Therefore, the solubility enhancements resulting from the presence of the DMSO cosolvent are obviously higher than those from ethanol.

Data Correlation. The new solubility data were correlated with the Chrastil equation,⁵⁹ which was developed on the basis of the complex formation of solute with solvent in the gas phase. The model was defined as

$$\ln(C/g \cdot dm^{-3}) = k \ln \rho/g \cdot dm^{-3} + a/(T/K) + b \quad (5)$$

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 solvate complex; ρ is the

density of supercritical fluid; T is equilibrium temperature; and a and b are constants. Since the concentrations of solute and cosolvent in the gas phase are relatively dilute, the densities of supercritical fluid mixtures were assumed as the values of pure carbon dioxide, which were taken from the NIST Chemistry WebBook.⁶¹ The Chrastil equation is linear in a log-log graph of solubility versus density. Table 6 gives the correlated results, and Figure 5 presents the comparisons of the calculated results with the experimental values for the system of $CO_2 + C.I.$ Disperse Violet 1. In general, the Chrastil equation correlated the equilibrium solubilities of C.I. Disperse Violet 1 to within about experimental uncertainty. As also seen from Table 6, the value of association number k is about 6 for the system without cosolvent. The values of k slightly decrease in the case of using ethanol as a cosolvent. However, those of k significantly decrease, down to about 3, as 5 mol % of DMSO was added. It could be attributed that stronger interactions between DMSO and C.I. Disperse Violet 1 lead to dramatically decreasing the association number of carbon dioxide with the dyestuff molecule.

The solubility data were also correlated with a semiempirical model of Mendez–Santiago and Teja,⁶⁰ which was derived by using a classical expansion of the Helmholtz energy around the critical point of the solvent to describe the mixture properties at infinite dilution. The Mendez–Santiago and Teja model was expressed as

$$(T/K) \ln(y_2 P/MPa) = A_1 + A_2 \rho/(mol \cdot cm^{-3}) + A_3(T/K)$$
(6)

where ρ is the density of solvent; y_2 is the mole fraction solubility of solute in supercritical fluid; and A_1 , A_2 and A_3 are parameters independent of *T* and *P*. Rearrangement of the above equation yields

$$(T/K) \ln(y_2 P/MPa) - A_3(T/K) = A_1 + A_2 \rho/(\text{mol} \cdot \text{cm}^{-3})$$
(7)

Mendez–Santiago and Teja⁶⁰ claimed that eq 7 could be used to check the consistency of experimental data. The experimental solubility data are considered consistently well, if all isotherms collapse to a single straight line on a graph of the left-hand side of eq 7 versus the density of solvent, ρ . This relationship is valid in the density ranges of 0.006 mol·cm⁻³ to 0.022 mol·cm⁻³. Figure 6 illustrates that all the experimental data follow the trend of linearity for the system of CO₂ + C.I. Disperse Violet 1. The correlated results from the Mendez– Santiago and Teja model are listed in Table 7. Although the average deviations from this model are slightly greater than those from the Chrastil equation, the deviations are still not far above the experimental uncertainty.

Conclusions

The dissolution of C.I. Disperse Violet 1 with supercritical carbon dioxide has been investigated with a semiflow apparatus under a wide range of contact time. A diffusion-controlled model represented well the experimental results, and the effective masstransfer coefficient was determined by fitting the extraction data to this simple mass-transfer model. The saturated solubilities of C.I. Disperse Violet 1 in supercritical carbon dioxide with or without cosolvents have also been measured in a temperature range of (353.2 to 393.2) K and pressures up to 30 MPa. The isothermal solubilities of C.I. Disperse Violet 1 in pure supercritical CO2 increased with increasing pressure, and crossover behavior was also found in $CO_2 + C.I.$ Disperse Violet 1 binary system. Either amphiprotic ethanol or aprotic DMSO has been used as a cosolvent to enhance dye's solubilities. Both cosolvents effectively increased the solubility of C.I. Disperse Violet 1, but DMSO induced greater solubility enhancement than ethanol. The Chrastil equation correlated the solubility data to about within the experimental uncertainty. The correlated results of the Mendez-Santiago and Teja model showed that the solubility data were consistent over the entire experiment conditions.

Acknowledgment

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