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Solubilities of C.I. Disperse Orange 25 and C.I. Disperse Blue 354 in Supercritical Carbon Dioxide

Takashi Shinoda and Kazuhiro Tamura*

Department of Chemistry and Chemical Engineering, Division of Applied Sciences, 40-20 Kodatsuno 2-chome,
Kanazawa University, Kanazawa, Ishikawa 920-8667, Japan

Solubilities of C.I. Disperse Orange 25 (3-[*N*-ethyl-4-(4-nitrophenylazo)phenylamino]propionitrile) and C.I. Disperse Blue 354 ([2-[[4-(dihexylamino)-2-methylphenyl]methylene]-1,1-dioxidobenzo[*b*]thien-3(2*H*)-ylidene]propanedinitrile) in supercritical carbon dioxide were measured by a flow-type apparatus. The solubility measurements were carried out at the temperature range from (323.15 to 383.15) K and the pressures from (10.0 to 30.0) MPa. The solubility of the dyes was examined in terms of pressure, temperature, and the density of supercritical carbon dioxide. An empirical equation was used to correlate the experimental solubilities of the dyes in terms of the density of carbon dioxide. Furthermore, the experimental data were represented successfully using a modified form of the PRSV (Peng−Robinson−Stryjek−Vera) EOS (equation of state), where vapor pressures and molar volumes of the dyes were calculated simultaneously.

Introduction

The wet-type dispersion method widely used for dyeing process of synthetic fabrics requires disperse agents and surfactants as well as a large amount of water to disperse dyes. After dyeing in the conventional dyeing process, the treatment of wastewater including various chemical additives and excess amounts of dyes is necessary and indispensable from an environmental viewpoint. To reduce the emission of environmental pollutants, waterless dyeing has been expected as an alternative method. Recently, a new dyeing process using supercritical carbon dioxide has been commented on with keen interest.[1,2] This new process is to be a potential alternative method with no requirement of water, additives, and drying process and also is capable of recovery and reuse of dyes. To develop and design the supercritical fluid dyeing process, we need the solubilities of the dyes and their accurate representation. Some research groups have reported experimental data[3−8] and proposed correlation methods using several equation of states.[4,9] In their calculation they evaluated vapor pressures of dyes by a conventional group contribution in place of the equation of state because of a shortage of experimental values at temperatures of interest. However, when there are no available group values for the group existing in the dyes due to their chemically complex structures, the group contribution method often fails to estimate the vapor pressures of the dyes. Therefore, we present an accurate representation of the solubilities of dyes using the vapor pressures and molar volumes of the dyes calculated simultaneously from an equation of state.

In this work, we measured the solubilities of two disperse dyes having complex structures in supercritical carbon dioxide. The reliability of the experimental values was examined by making a comparison of the solubilities of anthracene in supercritical carbon dioxide with the literature.[10−12] The experimental results of the dyes were correlated using the popular and conventional PR (Peng−Robinson) EOS[13] (equation of state), the PRSV (Peng−Robinson−Stryjek−Vera) EOS,[14] and a modified PRSV EOS proposed in this work. We calculated simultaneously the vapor pressures and molar volumes of the dyes as well as the fugacity coefficients of the dyes in the supercritical phase by means of the equations of state. Additionally, the results were compared with those calculated by using the PR and PRSV EOSs and by estimating the vapor pressures and molar volumes of the dyes from the group contribution method.

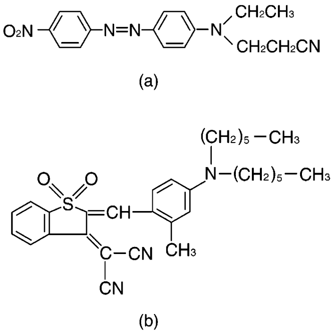

Figure 1. Chemical structures of C.I. Disperse Orange 25, (3-[*N*-ethyl-4-(4-nitrophenylazo)phenylamino]propionitrile; CAS number 31482-56-1), (a) and C.I. Disperse Blue 354, ([2-[[4-(dihexylamino)-2-methylphenyl]methylene]-1,1-dioxidobenzo[*b*]thien-3(2*H*)-ylidene]propanedinitrile), (b).

Experimental Section

Materials. C.I. Disperse Orange 25 (3-[*N*-ethyl-4-(4-nitrophenylazo)phenylamino]propionitrile; CAS number [31482−56−1]; purity 95−97%) was purchased from Aldrich Chemical. C.I. Disperse Blue 354 ([2-[[4-(dihexylamino)-2-methylphenyl]methylene]-1,1-dioxidobenzo[*b*]-thien-3-(2*H*)-ylidene]propanedinitrile; purity 95−97%) was kindly supplied by Clariant Japan. The chemical structures of the dyestuffs are shown in Figure 1. Impurity was checked by scanning the UV−visible wavelength from 190 nm to 1100 nm. The disperse dyes dissolved in ethanol did

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[*] Corresponding author. Fax: +81-76-234-4829. E-mail: tamura@t.kanazawa-u.ac.jp.

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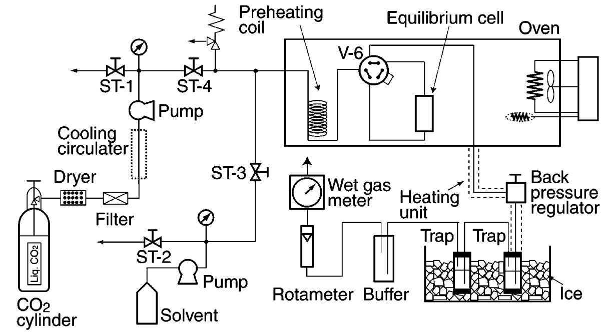

Figure 2. Schematic diagram of experimental apparatus.

not show any additives such as dispersing agents and surfactants and were used directly without further purification. Carbon dioxide (purity 99.9%) was obtained from Uno Sanso Co.

Apparatus and Procedure. A flow-type apparatus (SCF-201, JASCO) illustrated in Figure 2 was used to measure the solubility. Dyes were loaded in the equilibrium cell (150 mm long by 4.4 mm i.d.) packed with glass beads of 1 mm diameter to make a uniform flow distribution of the supercritical fluids. Both inlet and outlet sides of the equilibrium cell were filled with glass wool and plugged with a 0.2 μm pore filter to block the possible dye-powder entrainment. Temperature was controlled within ±0.1 K in the oven, and pressure was within ±0.2 MPa, controlled with the back-pressure regulator.

Carbon dioxide was delivered from the gas cylinder into the cell at a desired pressure by the circulation pump. A liquid carbon dioxide flow rate of 2.0 $\text{cm}^3\ \text{min}^{-1}$ was determined from preliminary experiments made at different flow rates of (1.0, 1.5, 2.0, 2.5, and 3.0) $\text{cm}^3\ \text{min}^{-1}$. After the carbon dioxide in the system reached the equilibrium pressure and temperature, a six-way valve was turned to flow the carbon dioxide into the cell. The line from the exit of the oven to the back-pressure regulator and cold-trap was temperature-controlled by a flexible heater to prevent it from clogging with dry ice or deposited dye in the flow lines. Dyes dissolved into supercritical carbon dioxide were collected by a two-step ice-cold trap filled with ethanol. Absorbance of the collected dye in solution was measured using a UV−visible spectrophotometer (BioSpec-1600, Shimadzu) with less than ±0.4% of absorbance, and the dye concentration was directly determined from the UV-absorbance of the dye. The solubility of the dye was calculated from the dye concentration and volumes of carbon dioxide measured by the wet gas meter (W-NK-1B, Shinagawa) within an accuracy of ±0.5%. After every experimental run, the whole apparatus was rinsed with acetone and ethanol, respectively. The solvents remaining in the line were completely recovered by inflowing carbon dioxide to the line heated at 373.15 K with an oven and a flexible heater.

Experimental Results

The solubilities of anthracene in supercritical carbon dioxide measured at 323.15 K were used to determine the reliability of the apparatus. Figure 3 shows a comparison of the solubilities of anthracene in supercritical carbon dioxide reported previously[10−12] with our experimental results. To compare the experimental solubilities measured at different conditions, we plotted the deviations between the experimental and calculated results obtained in fitting the PR EOS to our experimental values, which are defined by $\delta y_2 = y_2^{\text{exp}} - y_2^{\text{cal}}$. As shown in Figure 3, our results were in good agreement with the literature values.

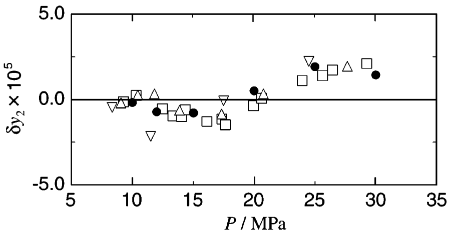

Figure 3. Comparison of solubility of anthracene, y_2, in supercritical carbon dioxide measured at 323.15 K with literature data: ●, this work; △, Johnston et al.;[10] □, Coutsikos et al.;[11] ▽, Hampson et al.[12]

Table 1. Solubility Data, y_2, of Dyes in Supercritical Carbon Dioxide

T = 323.15 K		T = 353.15 K		T = 383.15 K	
P/MPa	$10^7 y_2$	P/MPa	$10^7 y_2$	P/MPa	$10^7 y_2$
C.I. Disperse Orange 25					
10.0	0.1283	10.0	0.01956	10.0	0.08570
12.0	1.906	12.0	0.1424	12.0	0.2925
15.0	6.597	15.0	1.873	15.0	1.762
20.0	15.56	20.0	16.62	20.0	16.61
25.0	27.05	25.0	43.60	25.0	64.13
30.0	39.91	30.0	80.62	30.0	170.9
C.I. Disperse Blue 354					
10.0	0.2126				
12.0	6.290	12.0	0.1083	12.0	0.06711
15.0	31.62	15.0	3.152	15.0	0.7895
20.0	100.3	20.0	52.82	20.0	17.99
25.0	177.7	25.0	203.6	25.0	126.1
30.0	278.4	30.0	444.8	30.0	409.5

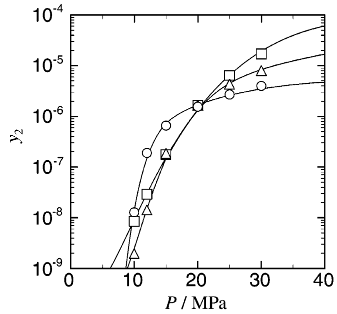

Figure 4. Solubility of C.I. Disperse Orange 25 in supercritical carbon dioxide at different temperatures: ○, 323.15 K; △, 353.15 K; □, 383.15 K; —, calculated by the modified PRSV EOS.

The solubility measurements of C.I. Disperse Orange 25 and C.I. Disperse Blue 354 were carried out at the temperature range from (323.15 to 383.15) K and pressures from (10.0 to 30.0) MPa. The experimental results listed in Table 1 were obtained from an arithmetic mean value of several measurements. The reproducibility of these solubilities was within ±5% in mole fraction. The experimental data of C.I. Disperse Orange 25 and C.I. Disperse Blue 354 at (323.15, 353.15, and 383.15) K are given in Figures 4−7. Figures 4 and 5 show the solubilities of the dyes in terms of pressure and temperature. The solubility curves intersect each other at ≈20 MPa for C.I. Disperse Orange 25 shown in Figure 4 and around 25 MPa for C.I. Disperse Blue 354 in Figure 5. The solubilities of the dyes increase as the pressure increases monotonically at a fixed temperature. However, compared with the temperature increments, the solubilities of the dyes change inversely at the intersection indicated in Figures 4 and 5. This solubility behavior at a fixed pressure results from the coincidence of decreasing the density of carbon dioxide and increasing the vapor pressures of the dye at the increment

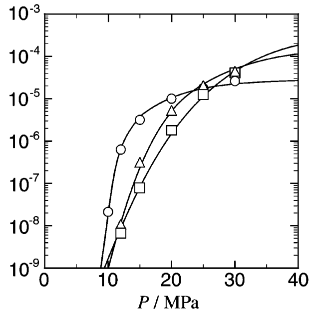

Figure 5. Solubility of C.I. Disperse Blue 354 in supercritical carbon dioxide at different temperatures: ○, 323.15 K; △, 353.15 K; □, 383.15 K; —, calculated by the modified PRSV EOS.

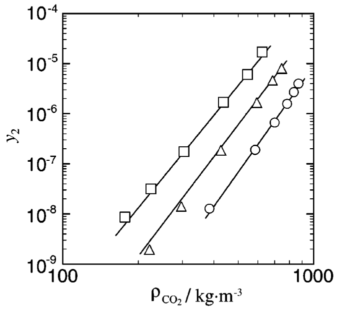

Figure 6. Solubility of C.I. Disperse Orange 25 versus density of carbon dioxide: ○, 323.15 K; △, 353.15 K; □, 383.15 K; —, calculated by eq 1.

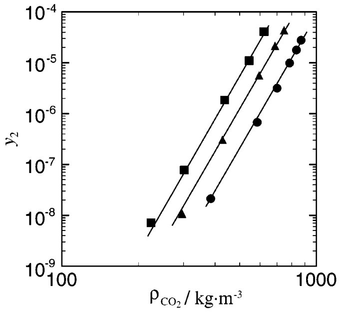

Figure 7. Solubility of C.I. Disperse Blue 354 versus density of carbon dioxide: ●, 323.15 K; ▲, 353.15 K; ■, 383.15 K; —, calculated by eq 1.

of the temperature. Figures 6 and 7 depict the solubilities of the dyes as a function of the density of supercritical carbon dioxide. Obviously, the logarithmic function of solubilities for every isotherm increases linearly as the density of carbon dioxide increases.

Empirical Correlation of Solubility Data. The solubilities of disperse dyes in supercritical carbon dioxide were correlated using an empirical equation proposed by Sung and Shim.[5]

$$\ln y_2 = a + b/T + (c + d/T) \ln \rho \tag{1}$$

where y_2 is the mole fraction of dye and ρ is the density of supercritical carbon dioxide, calculated from the equation of state which can describe the $P-V-T$ behavior accurately at the temperature range from the triple point to 1100 K and the pressure range up to 800 MPa.[15] The values of a, b, c, and d were obtained by fitting eq 1 to the experimental results. The constants in eq 1 and the absolute relative deviation for the dye solubilities for the three isotherms are summarized in Table 2. The solubilities of C.I. Disperse Orange 25 and C.I. Disperse Blue 354 calculated by eq 1 were compared with the experimental values in Figures 6 and 7, respectively. Good agreement between the experimental and calculated solubilities of the disperse dyes was obtained.

Table 2. Constants in Eq 1

	parameter				
system	a	b/K^{-1}	c	d/K^{-1}	AAD%[a]
CO_2 + C.I. DO 25	1.7376	−20129	1.1637	1914.1	13.12
CO_2 + C.I. DB 354	−48.940	−6721.2	8.8658	−40.467	10.58

[a] $\text{AAD\%} = (1/ND)[\sum_{i=1}^{ND}|\{y_{2,i}^{\text{exp}} - y_{2,i}^{\text{cal}}\}/y_{2,i}^{\text{exp}}| \times 100]$.

Table 3. Critical Constants (T_c, P_c) and Acentric Factor (ω) for the Dyes Used in This Work

compound	T_c[a]/K	P_c[a]/MPa	ω[b]
C.I. Disperse Orange 25	871.0	1.703	1.2144
C.I. Disperse Blue 354	866.0	1.112	0.9245

[a] Estimated by the Miller method. [b] Estimated by the Lee−Kesler method.

Calculated Results

Under the reasonable assumptions that no solvent dissolves in the solid phase, the solid solute is incompressible, and its vapor pressure is very low, the solubility of a solid (component 2) in supercritical carbon dioxide (component 1) is expressed as

$$y_2 = \frac{P_2^{\text{sat}} \exp[V_2^{\text{S}}(P - P_2^{\text{sat}})/RT]}{\phi_2^{\text{SCF}} P} \tag{2}$$

where V_2^{S} is the molar volume of dye and P_2^{sat} is the saturated vapor pressure of dye. The fugacity coefficient of dye in the supercritical phase ϕ_2^{SCF} was calculated using an EOS by the thermodynamic relationship.[16] At the beginning we adopted an original version of the PR and PRSV EOSs, whose expressions are described elsewhere.[13,14] The critical constants and acentric factor of the dyes were estimated by group contribution methods. The Miller method[17] for the critical temperature and critical pressure, and the Lee−Kestler method[16] for the acentric factor were used. The estimated values are given in Table 3. We evaluated the vapor pressures of the dyes by the Lee−Kestler equation using the acentric factor and the molar volume of the dyes by the group contribution method of Yamamoto et al.[18] To represent the solubilities of dyes in supercritical carbon dioxide, we used a van der Waals mixing rule associated with the binary interaction parameter k_{ij}, expressed as follows.

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \tag{3}$$

The binary interaction parameter k_{ij} was obtained by minimizing the following objective function Q.

$$Q = \frac{1}{ND} \sum_{i=1}^{ND} \left(\frac{y_{2,i}^{\text{exp}} - y_{2,i}^{\text{cal}}}{y_{2,i}^{\text{exp}}} \right)^2 \tag{4}$$

where ND is the number of experimental data and $y_{2,i}$ is the solubility of the dye in the supercritical phase. As an example, Figure 8 shows poor agreement between the experimental results for C.I. Disperse Orange 25 at 383.15 K and those calculated by the PR and PRSV EOSs. When the vapor pressures of the dyes are estimated using the Lee−Kestler method, the solubilities of the dyes cannot be correlated at all using the fugacity coefficients calculated

Table 4. Estimated Vapor Pressure (P^{sat}) and Molar Volume (V^S) of Dyes

		P^{sat}/Pa				10^6V^S/m^3·mol^{-1}			
compound	T/K	Lee−Kestler	PR	PRSV	modified PRSV	Yamamoto et al.	PR	PRSV	modified PRSV
C.I. Disperse Orange 25	323.15	1.0×10^{-5}	3.4×10^{-5}	1.4×10^{-8}	2.3×10^{-7}	261	346	343	344
	353.15	6.8×10^{-4}	1.9×10^{-3}	5.0×10^{-6}	4.7×10^{-6}	261	349	345	345
	383.15	2.1×10^{-2}	4.8×10^{-2}	5.5×10^{-4}	1.0×10^{-4}	261	352	348	347
C.I. Disperse Blue 354	323.15	4.5×10^{-4}	9.0×10^{-4}	4.9×10^{-11}	2.8×10^{-9}	448	531	519	521
	353.15	1.5×10^{-2}	2.5×10^{-2}	1.1×10^{-7}	4.7×10^{-8}	448	536	523	523
	383.15	2.5×10^{-1}	3.9×10^{-1}	4.7×10^{-5}	1.4×10^{-6}	448	448	528	525

Table 5. Correlation of Solubility of Dyes (2) in Supercritical Carbon Dioxide (1) with the PR EOS, PRSV EOS, and Modified PRSV EOS

		PR EOS		PRSV EOS			modified PRSV EOS		
system	T/K	k_{12}	AAD%[a]	k_{12}	κ_1	AAD%[a]	k_{12}	κ_1[b]	AAD%[a]
CO_2 + C.I. Disperse Orange 25	323.15	0.344	82.2	0.162	0.848	32.3	0.196	0.476	9.2
	353.15	0.608	83.2	0.174	0.848	14.3	0.168	0.860	13.4
	383.15	0.756	82.3	0.237	0.848	56.0	0.140	1.244	7.9
CO_2 + C.I. Disperse Blue 354	323.15	0.467	83.4	0.114	2.216	34.1	0.142	1.714	12.2
	353.15	0.651	80.1	0.130	2.216	12.1	0.121	2.362	10.8
	383.15	0.927	80.1	0.281	2.216	76.1	0.100	3.010	7.9

[a] AAD% = $(1/ND)[\sum_{i=1}^{ND}|\{y_{2,i}^{exp} - y_{2,i}^{cal}\}/y_{2,i}^{exp}| \times 100]$. [b] κ_1 in the modified PRSV EOS was calculated using eq 5 at each temperature.

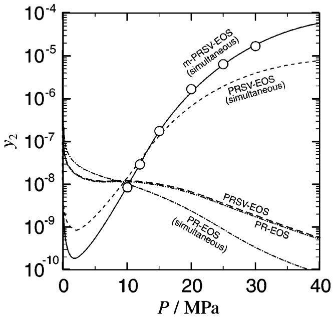

Figure 8. Solubility of C.I. Disperse Orange 25 in supercritical carbon dioxide at 383.15 K: —, P_2^{sat} and V_2^S calculated simultaneously by the modified PRSV EOS; - · -, PRSV EOS; - - -, PR EOS; — — —, PRSV EOS with P_2^{sat} estimated by the Lee−Kestler method and V_2^S by the Yamamoto et al. method; - · · -, PR EOS with P_2^{sat} estimated by the Lee−Kestler method and V_2^S by the Yamamoto et al. method.

by the PR and PRSV EOSs and show no difference between both calculated results in Figure 8. Neau et al.[19] pointed out that the vapor pressure of solids is very sensitive to the calculation of the solubilities of the solids in supercritical fluids. However, the experimental vapor pressures of the solidlike dyes and a reliable estimation method for their complex dye structures have not yet been available. So we present an alternative method to calculate the vapor pressures of the dyes using an EOS in place of the Lee−Kestler method. To improve the representation of vapor pressures of pure compounds from low reduced temperatures to critical points, Stryjek and Vera[15] assumed that the parameter for pure compounds κ, being only a function of the acentric factor, can be expressed in terms of the parameters κ_0 and κ_1. The κ_0 was given by a cubic function of the acentric factor, and the κ_1 was fixed as independent of temperature. In the present work we proposed a modified form of the PRSV EOS, further taking into account the temperature dependence of κ_1 for a precise estimation of the vapor pressures of the dyes over a wide range of temperatures. Using the PR, PRSV, and modified PRSV EOSs, we calculated simultaneously the vapor pressures and molar volumes of the dyes as well as the fugacity coefficients of the dyes from the solubility correlation. The adjustable parameter κ_1 of the dyes in the PRSV and modified PRSV EOSs as well as the binary interaction parameter k_{ij} were obtained fitting the models to the solubilities of the dyes in supercritical carbon dioxide by minimizing the objective function Q defined by eq 4. The vapor pressures, molar volumes, and fugacity coefficients of the dyes calculated simultaneously from the solubility correlation of the dyes were determined using the EOS to satisfy the equality of chemical potentials in both solid and vapor phases. Figure 8 compares the experimental results for C.I. Disperse Orange 25 at 383.15 K with those calculated by the PR, PRSV, and modified PRSV EOSs. The solubilities of the dyes calculated by the PR, PRSV, and modified PRSV EOSs depend on the models. The modified PRSV EOS makes the most significant improvement to the calculation results. This is possibly because the modified PRSV EOS, taking into account the temperature dependence for the parameter κ_1, can represent the vapor pressure more reasonably than the PR and PRSV EOSs. Table 4 presents the vapor pressures and molar volumes of the dyes obtained from the solubility correlations by using the PR, PRSV, and modified PRSV EOSs. However, we cannot make a comparison between these experimental and calculated values because there are no experimental results for the dyes. The absolute relative deviations of the solubilities of the dyes between the experimental and calculated results are summarized in Table 5, along with the binary interaction parameter k_{ij} and adjustable parameter κ_1. The solubility of dyes in supercritical carbon dioxide at every temperature can be correlated with good accuracy using the modified PRSV EOS with the temperature-dependent parameter κ_1 given in Table 6. The constants κ_2 and κ_3 were determined from a linear plot of κ_1 against the reduced temperature T_r, as shown in Figure 9.

Table 6. Coefficients in Eq 5

compound	κ_2	κ_3
C.I. Disperse Orange 25	−3.657	11.14
C.I. Disperse Blue 354	−5.276	18.73

$$\kappa_1 = \kappa_2 + \kappa_3 T_r \tag{5}$$

Additionally, the binary interaction parameter k_{ij} in Table 7 can be expressed by a linear function of temperature in terms of the constants A_0 and A_1, as shown in Figure 10.

$$k_{ij} = A_0 + A_1 T \tag{6}$$

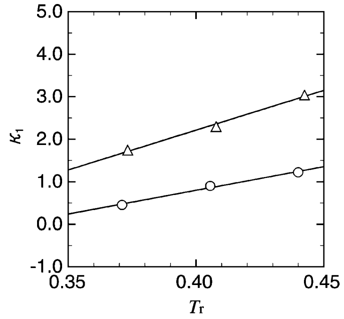

Figure 9. PRSV parameters of disperse dyes used in the modified PRSV EOS, κ_1, plotted versus reduced temperature: ○, C.I. Disperse Orange 25; △, C.I. Disperse Blue 354; —, correlated by eq 5.

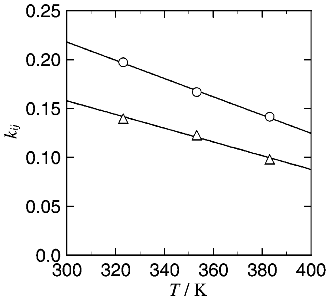

Figure 10. Binary interaction parameter of dyes, k_{ij}, plotted versus temperature: ○, C.I. Disperse Orange 25; △, C.I. Disperse Blue 354; —, correlated by eq 6.

Table 7. Coefficients in Eq 6

system	A_0	$10^4 A/\mathrm{K}^{-1}$
CO_2 + C.I. Disperse Orange 25	0.4975	−9.322
CO_2 + C.I. Disperse Blue 354	0.3683	−7.015

Using these temperature-dependent parameters κ_1 and k_{ij} calculated from eqs 5 and 6 with the constants given in Tables 6 and 7, we can interpolate successfully the solubilities of the disperse dyes at the temperatures (323.15 to 383.15) K and the pressures from (10.0 to 30.0) MPa, as shown in Figures 4 and 5.

Conclusions

Solubilities of the dyes C.I. Disperse Orange 25 and C.I. Disperse Blue 354 in supercritical carbon dioxide have been measured in the temperature range from (323.15 to 383.15) K and at pressures from (10.0 to 30.0) MPa. The solubilities of the disperse dyes in supercritical carbon dioxide were correlated accurately in terms of the density of carbon dioxide using an empirical equation of Sung and Shim. Furthermore, the experimental results were correlated with good accuracy using a modified PRSV EOS with a linear function of temperature for the binary interaction parameter. The vapor pressures and molar volumes of dye calculated from the modified PRSV EOS simultaneously may be evaluated reasonably in the case of the experimental vapor pressures and molar volumes being not available.

Acknowledgment

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