Measurement and Correlation of Solubilities of Some Disperse Azo Dyes in Supercritical Carbon Dioxide

Mohammad Hojjati,[†] Yadollah Yamini,[*,†] Mostafa Khajeh,[‡] Shohre Rouhani,[§] and Kamaladin Gharanjig[§]

Department of Chemistry, School of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran, Department of Chemistry, University of Zabol, P.O. Box 98615-538, Zabol, Iran, and Department of Organic Colorants, Institute for Colorants, Paint and Coatings (ICPC), P.O. Box 16765-654, Tehran, Iran

The solubilities of three novel disperse azo dyes, ethyl 2-[6-{(*E*)-2-[4-(diethylamino)-2-methylphenyl]-1-diazenyl}-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl] acetate (Dye 1), ethyl 2-[6-{(*E*)-2-3-hydroxy-2-naphthyl-1-diazenyl}-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl] acetate (Dye 2), and 6-{(*E*)-2-[4-(diethylamino)phenyl]-1-diazenyl}-2-propyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (Dye 3), in supercritical carbon dioxide were measured at $T = (308, 318, 328, 338, \text{and } 348)$ K and various pressures in the range of (122 to 355) bar. The measurements were performed using a simple static method. On the basis of the obtained experimental results, the solubilities increased by increasing the density of supercritical CO_2. Also, the solubilities of the dyes in supercritical CO_2 at high pressure were decreased in the order of Dye 3 > Dye 1 > Dye 2, which parallels the order of their relative melting points. The higher the melting point, the lower the solubility. The mole fraction solubilities, y_2, and solubilities, s, of the disperse dyes ranged from $[(0.01 \text{ to } 20.7)\cdot 10^{-6}$ and $(0.01 \text{ to } 15.8)\cdot 10^{-2}]\ \text{g}\cdot\text{L}^{-1}$, respectively. The solubility data were correlated using a semiempirical density-based Chrastil model with an overall average absolute relative deviation of 18.6 %. Using the correlation results, the enthalpy of CO_2-dye solvation approximated in the range of (29 to 225) $\text{kJ}\cdot\text{mol}^{-1}$ for different dyes. The calculated results show satisfactory agreement with the experimental data.

Introduction

Supercritical fluid dyeing (SFD) technology has received attention in the textile industry due to increasing environmental concerns, as reflected by a number of research communications dedicated to this field.[1–7]

SFD is an alternative dyeing process, which is able to replace the conventional wet process. In this process, water, surfactants, dispersing agents, and the drying process are eliminated. Therefore, this method will not deliver a lot of wastewater to the environment. Moreover, energy (roughly 50 %) can be saved.[8,9] However, to apply this technique, the knowledge of the solubility of suitable dyes for textiles in supercritical carbon dioxide (SC-CO_2) is required. Solubility measurements of some dyes in SC-CO_2 have been reported.[10,11] These results are commonly correlated using theoretical or semiempirical models.[12–16]

Experimental solubilities of dyes in SC-CO_2 are the most important parameters for selecting dyes and for predicting optimum temperature and pressure for the dying process. Thus, solubility data are needed for the development of the supercritical dyeing processes. In the present study, solubilities of three novel disperse azo dyes, 2-[6-{(*E*)-2-[4-(diethylamino)-2-methylphenyl]-1-diazenyl}-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl] acetate (Dye 1),[17] ethyl 2-[6-{(*E*)-2-3-hydroxy-2-naphthyl-1-diazenyl}-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl] acetate (Dye 2),[18] and 6-{(*E*)-2-[4-(diethylamino)phenyl]-1-diazenyl}-2-propyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (Dye 3),[19] have been determined over a range of pressures and temperatures. The experimental solubility data were correlated using a semiempirical density-based Chrastil model in supercritical carbon dioxide.

Experimental Section

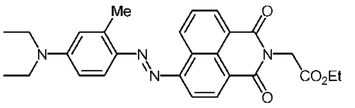
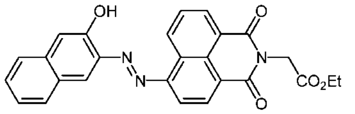
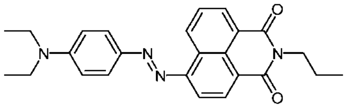
Apparatus and Operation. All solubility measurements were performed using a Suprex (Pittsburgh, PA) MPS/225 system equipped with a modified static system in supercritical fluid extraction (SFE) mode. A detailed description of the construction and calibration of the system has been previously reported.[20] To prevent channeling, briefly, a 1 mL high-pressure saturation cell was filled with a mixture of clean glass beads and 100 mg of the dye. The saturation cell was placed in the oven of the system to provide precise temperature control (± 0.2 K) during the solubility determination. A syringe pump was used in the constant pressure (± 1 bar) mode to supply pressurized CO_2 into the saturation cell. When the equilibrium at the desired temperature and pressure was reached (40 min), a 102 μL portion of the saturated supercritical CO_2 was loaded into the injection loop. It should be noted that by monitoring solubility data versus time, 40 min was found to be adequate to ensure the attainment of equilibrium. The loop was then depressurized into the collection vial containing dichloromethane. Finally, the sample loop was washed with dichloromethane and was collected in the collection vial. The final volume of the solution was adjusted to 5 mL. Solubility determinations were performed at temperatures ranging from (308 to 348) K and pressures from (122 to 355) bar. During a typical experiment, the oven temperature and SC-CO_2 pressure were held constant. The solubilities were determined by absorbance measurements at a suitable wavelength (λ) for each compound (Table 1) using a

---

[*] Corresponding author. Tel.: +98 21 88006631. Fax: +98 21 88006544. E-mail: yyamini@modares.ac.ir.
[†] Tarbiat Modares University.
[‡] University of Zabol.
[§] Institute for Colorants, Paint and Coatings (ICPC).

10.1021/je7003534 CCC: $40.75

Table 1. Structure of Dyes and Their Physicochemical Properties

Compound	Chemical Formula	MW/g·mol^{-1}	T_m/K	Chemical Structure	λ_{max}/nm
Dye 1	$C_{27}H_{28}N_4O_4$	472.55	568-569		543
Dye 2	$C_{26}H_{19}N_3O_5$	453.46	650-651		520
Dye 3	$C_{25}H_{26}N_4O_2$	414.51	555-556		537

model 2100 Shimadzu UV–vis spectrophotometer. Stock solutions of the solid samples were prepared by dissolving appropriate amounts of the solid samples in dichloromethane. A set of five standard solutions were then prepared by appropriate dilution of the stock solution. The calibration curves obtained (with regression coefficients better than 0.999) were used to establish the concentration of the dyes in the collection vial. The mole fraction compositions of the solutes were obtained with percent relative standard deviation less than ± 9 %.

Materials. Carbon dioxide (99.99 %) was purchased from Sabalan Co. (Tehran, Iran). HPLC grade dichloromethane was obtained from Merck (Darmstadt, Germany) and was used as received. The novel disperse azo dyes were synthesized and purified as described before.[17–19] The purities of the azo dyes were confirmed by spectroscopic data and elemental analysis. The mass fraction purities of the dyes were greater than 99 %. However, prior to the measurement of solubilities, the dyes were extracted by dynamic SFE at $P = 253$ bar and $T = 328$ K for a duration of 20 min at the supercritical flow rate of 0.5 mL·min^{-1}. The impurities were only present during the extraction of the first (2 to 4) % of the material charged into the extraction vessel. After making sure that no impurities existed in the extract, solubility measurements were made. Some basic information for these disperse azo dyes is given in Table 1, in which T_m is the melting point that was measured using a melting point measurement instrument from SANYO Gallenkamp PLC Company (Leicestershire, U.K.).

Results and Discussion

Experimental Solubility Data. The reliability and efficiency of the solubility measurement apparatus were previously established by measuring the solubility of naphthalene in SC-CO_2 at 308 K and at different pressures. The measured mole fraction solubilities of naphthalene were (11.6, 14.2, 16.2 and 17.4)·10^{-3} for P = (105.6, 136.2, 165.8, and 201.3) bar, respectively, and agreed within approximately 8 % to 6.8 % with those of previous measurements.[20]

Solubility measurements of disperse dyes with a static apparatus have shown that the spectrophotometric determination of concentrations is affected by even small concentrations of more soluble impurities absorbing in the same range of the spectrum as the dyes itself.[21] The flowing method often allows an easy extraction of such impurities; the continuous purification can be continued until a constant shape of the spectrum is observed for the collected extracts. Thus, in the present work, small quantities of volatile impurities present were extracted by dynamic SFE, prior to the measurement of solubility.

The experimental results are listed in Table 2 in terms of equilibrium mole fraction, y_2 and s/g·L^{-1}, of the solute in supercritical CO_2. The mole fraction solubilities of the disperse dyes ranged from (1.5 to 11.4)·10^{-6}, (0.01 to 5.7)·10^{-6}, and (0.1 to 20.7)·10^{-6} for Dye 1, Dye 2, and Dye 3, respectively.

Each reported data point is the average of at least three replicate measurements with relative standard deviations of less than 9 %. Examination of the solubility data in Table 2 reveals that the solubility of disperse dyes increases with an increase in pressure, at all temperatures. This is due to the increase of CO_2 density with increasing pressure, which happens since CO_2 density is directly related to the dissolving power of CO_2. This effect is due to the decrease of the intermolecular distance, so the solute–solvent interactions increase.[22]

The solubility behavior with temperature is more complex. However, despite the decreased density of CO_2 at higher temperatures (at constant pressures), the influence of pressure on the solubility is more pronounced at higher temperatures. The data given in Table 2 clearly reveal that, at a constant temperature, increasing the density (by increasing pressure) enhances the solubility, and the increase in density at a constant pressure (by lowering temperature) diminishes the solubility. Similar observations have already been reported in the literature.[23] By examining the effect of temperature on the solubilities (Table 2), we find the existence of a retrograde (crossover pressure effect) behavior for all three dyes at about 160 bar. It is worth pointing out that the crossover point is difficult to see from Table 2, but it can be easily observed from the mole fractions versus pressure isotherms (Figure 1). Two competing effects can explain this effect. In principal, increasing temperature favors solubility via an increase in vapor pressure of the dye, but at the same time, the solvent density decreases. At low pressures, the decrease of solvent density dominates, and the overall solubility of the dye decreases with increasing temperature. At higher pressures, the solubilities increase with rising

Table 2. Solubilities of Dye 1, Dye 2, and Dye 3 in SF-CO_2 at Various Temperatures and Pressures

			Dye 1		Dye 2		Dye 3	
			100s		100s		100s	
T/K	P/bar	ρ/g·L^{-1}	g·L^{-1}	10^6y	g·L^{-1}	10^6y	g·L^{-1}	10^6y
308	122	771	2.5	3.1	–	–	0.4	0.5
	152	818	3.1	3.5	–	–	0.5	0.6
	182	850	2.9	3.2	–	–	0.6	0.8
	213	876	3.0	3.2	0.00_1	–	0.8	0.9
	243	897	2.8	2.9	0.00_3	–	0.9	1.0
	274	916	2.9	3.0	0.00_5	0.01	1.0	1.1
	304	931	2.9	2.9	0.00_7	0.01	1.1	1.3
	334	946	3.0	3	0.01_5	0.02	1.2	1.4
	355	955	3.3	3.2	0.02_1	0.02	1.3	1.5
318	122	661	1.9	2.7	–	–	0.2	0.4
	152	745	2.4	3.0	–	–	0.6	0.9
	182	792	3.0	3.6	0.00_1	–	1.0	1.3
	213	826	3.4	3.9	0.00_4	–	1.3	1.7
	243	852	3.8	4.2	0.01	0.01	1.7	2.1
	274	875	4.0	4.2	0.03	0.03	1.9	2.3
	304	893	4.1	4.3	0.06	0.07	2.2	2.6
	334	910	4.3	4.4	0.09	0.10	2.5	3.0
	355	919	4.7	4.8	0.13	0.13	2.9	3.3
328	122	516	1.1	2.0	–	–	0.1	0.2
	152	657	2.2	3.1	–	–	0.6	0.9
	182	726	3.1	4.0	0.00_1	–	1.2	1.8
	213	771	3.9	4.7	0.00_8	0.01	2.0	2.7
	243	804	4.4	5.2	0.03	0.04	2.6	3.5
	274	831	5.0	5.6	0.06	0.07	3.4	4.3
	304	853	5.3	5.8	0.20	0.23	4.1	5.1
	334	872	5.6	6.0	0.41	0.46	4.7	5.7
	355	884	6.1	6.4	0.66	0.72	5.4	6.5
338	122	396	0.7	1.6	–	–	0.1	0.1
	152	561	1.5	2.5	–	–	0.4	0.8
	182	654	2.9	4.2	0.00_1	–	1.3	2.2
	213	712	4.1	5.3	0.01_2	0.02	2.6	3.9
	243	754	5.0	6.2	0.09	0.11	3.8	5.4
	274	786	6.0	7.1	0.24	0.29	5.3	7.1
	304	812	6.5	7.4	0.56	0.67	6.9	9.0
	334	834	7.0	7.9	1.54	1.80	8.4	10.6
	355	848	7.8	8.6	2.67	3.05	9.5	11.9
348	122	327	0.5	1.5	–	–	0.1	0.2
	152	477	1.0	2.0	–	–	0.4	0.8
	182	585	2.8	4.5	0.00_1	–	1.4	2.6
	213	652	4.1	5.8	0.01_5	0.02	3.1	5
	243	702	5.4	7.2	0.11	0.16	5.3	8
	274	740	6.6	8.3	0.53	0.69	7.6	10.9
	304	772	7.7	9.3	1.45	1.82	10.3	14.2
	334	796	8.6	10	3.69	4.50	12.7	17
	355	811	10	11.4	4.78	5.72	15.8	20.7

temperatures because the densities in this range only slightly depend on temperature and the normal temperature dependence of solubility dominates. The existence of a crossover pressure in solid supercritical fluid systems has been suggested to indicate the reliability and consistency of experimental solubility data.[24]

The results obtained in this study indicate that the solubility of dyes at high pressure vary in the order Dye 3 > Dye 1 > Dye 2. The exchange of the carbonyl group in Dye 1 by the CH_2 group results in a significant solubility enhancement of Dye 3 in comparison with Dye 1. Similar results have been reported in the literature.[23,25] The ability to form either inter- or intramolecular hydrogen bonds promotes mutual solute interactions, and consequently, the solubilization in CO_2 is hindered.[23] It is presumed that the intermolecular hydrogen bonds are responsible for poor solubility of Dye 2 in SF-CO_2. It is worth noting that the description between the solubility and molecular interaction is ambiguous. We expect the correlation results obtained in terms of the Chrastil empirical model to give a solution of the molecular interactions of dyes in SC-CO_2.

Correlation of Experimental Solubility Data. In the present study, to check the accuracy of the predicted solubilities based on correlation equations, the objective function used is the average absolute relative deviation (AARD) between the calculated and experimental solubility

$$\text{AARD} = \frac{1}{N}\sum_{i=1}^{N}\frac{|S_{\text{calcd}} - S_{\text{exptl}}|}{S_{\text{exptl}}} \tag{1}$$

where N is the number of experimental data points. The S_{exptl} and S_{calcd} are experimental and calculated solubility values, respectively. A single least-squares process was used to correlate data obtained by the models over the ranges of experimental pressures and temperatures. To correlate the dye solubility with the density-based models, the density of pure SC-CO_2 (ρ) at pressures and temperatures of interest should be known. In this work, the ρ values of SC-CO_2 were calculated by the computer system of the Suprex MPS/225 at various pressures and temperatures. It is worth noting that the Suprex MPS/225 uses the modified equation of state extended to include high-pressure fluids as proposed by Pitzer[26] and Pitzer et al.[27]

The accurate knowledge of the equilibrium solubility of the materials to be processed in the selected SCF solvent and/or the solubility of that SCF in those materials are key factors affecting the efficacy and the corresponding technical and economical success of most SCF processes. Therefore, if solubility of the solid in SCF is not completely determined experimentally, it must be obtained and extended by fitting and correlating theoretical or semiempirical models to the existing experimental data. Thus, equations of state (EOS) are the most widely used models to correlate and predict solid-SCF equilibrium.[28] However, even simple and more general cubic EOSs usually are required to fit model parameters and pure solute properties. Usually these properties are frequently unavailable in the literature, especially for pharmaceutical compounds, polymers, dye molecules, and biomolecules.[29–31]

To avoid some of these disadvantages as well as more complicated computational routines, most authors try to use more simple semiempirical correlations such as Chrastil's model,[32] which correlates the solubility of a solute, in a supercritical solvent, to the density and temperature. This model is based on the hypothesis that one molecule of solute, A, associates with k molecules of solvent, B, to form a solvate complex AB_k, in equilibrium with the system. The definition of the equilibrium constant, obtained through several thermodynamic considerations, leads to the following expression for the solid solubility

$$s/\text{g}\cdot\text{L}^{-1} = (\rho/\text{g}\cdot\text{L}^{-1})^k \exp(a/(T/\text{K}) + b) \tag{2}$$

where s is the solubility of Dye in SC-CO_2; ρ is the density of the pure CO_2 at the experimental absolute temperature T and pressure P. The constant, k, expresses an average equilibrium association number, which is a characteristic constant for a given gas−solute system. The parameter a is defined as $\Delta H/R$, where R is the universal gas constant and ΔH is the sum of the enthalpies of vaporization and solvation. Finally, the parameter b is dependent on the molecular weights of solvent and solute.

The logarithmic solubility−density relationship shows a linear behavior for all the isotherms, as is illustrated in Figure 2. By performing a multiple linear regression on ln s as a function of ln ρ and $1/T$, one obtains k = (1.8, 28.1, and 6.2), a = (−3203, −28155, and −9833) K, and b = (−20.2, −206.6, and −43.3) for Dye 1, Dye 2, and Dye 3, respectively (Table 3).

The thermodynamic quantity, ΔH, can be calculated directly from a, resulting, for the studied system, in values of (−29.04,

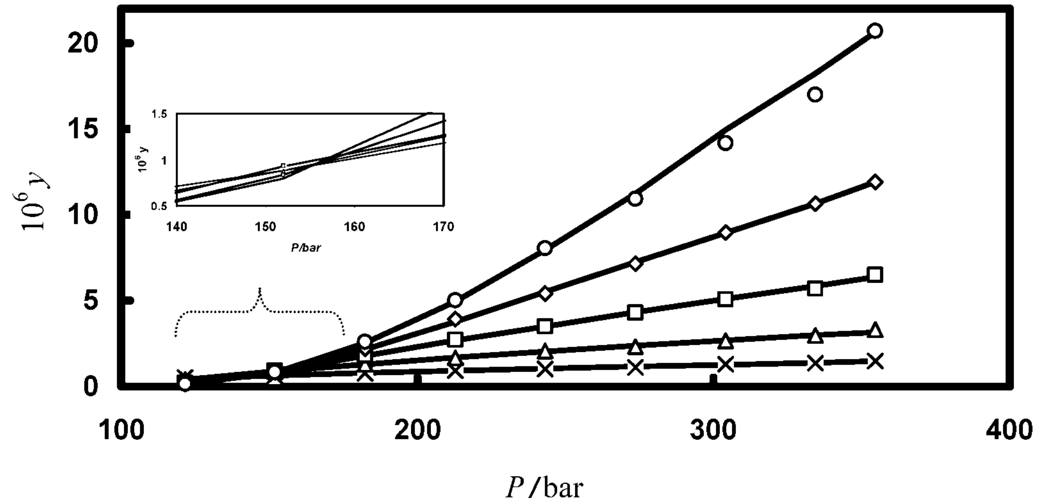


Figure 1. Equilibrium mole fraction of Dye 3 as a function of pressure. Lines represent experimental and points represent theoretical data: ×, 308 K; Δ, 318 K; □, 328 K; ◇, 338 K; ○, 348 K.

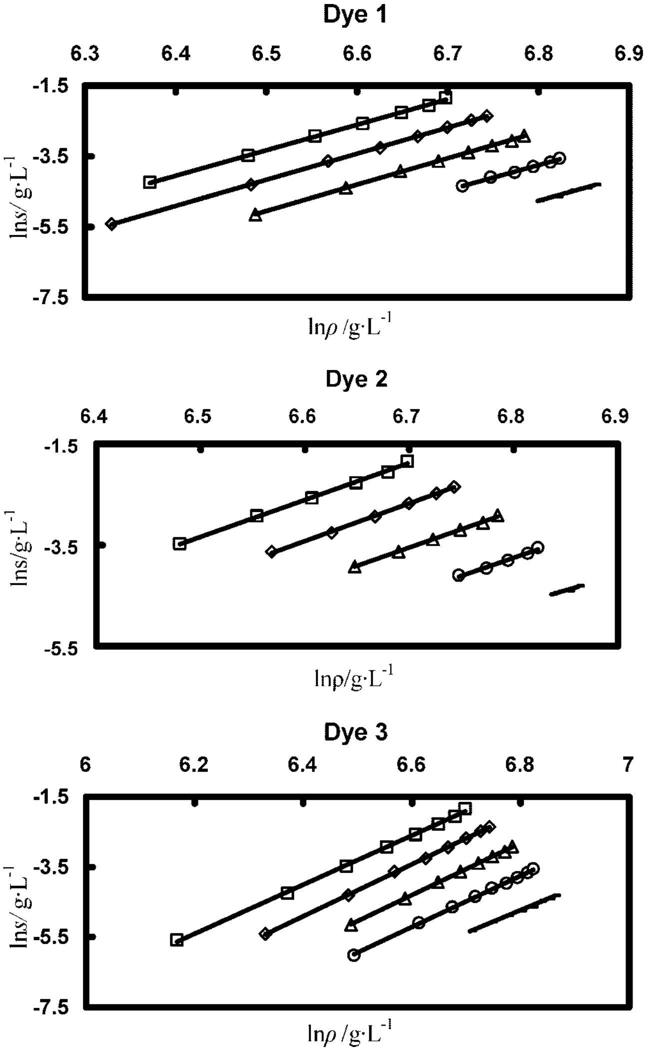


Figure 2. Logarithmic relationship between the solubility of the dyes and the density of supercritical CO_2 at (308, 318, 328, 338, and 348) K. Lines represent Chrastil's regression fit: –, 308 K; ○, 318 K; Δ, 328 K; ◇, 338 K; □, 348 K.

−225.3, and −82.2) kJ·mol^{-1} for Dye 1, Dye 2, and Dye 3, respectively. The average absolute relative deviations of the fitted Chrastil equation from experimental data were calculated to be 15.2 %, 17.3 %, and 23.4 % for Dye 1, Dye 2, and Dye 3, respectively.

Table 3. Solubility Constants of the Chrastil Model for Dye 1, Dye 2, and Dye 3 in Supercritical CO_2

Dye	*b*	*k*	*a*/K	100·AARD
Dye 1	−20.2	1.8	−3203	15.2
Dye 2	−206.6	28.1	−28155	17.3
Dye 3	−43.3	6.2	−9833	23.4
			average	18.6

Conclusions

Equilibrium solubilities of Dyes in supercritical CO_2 were measured by a static analytical method, in the pressure range from (122 to 355) bar at (308, 318, 328, 338, 348, and 358) K. Equilibrium solubility data, expressed in terms of Dyes' mole fraction, range from $(0.02 \text{ to } 20.7) \cdot 10^{-6}$, with a relative standard deviation of 9 %. At a constant temperature, the solvent capacity to dissolve dyes increases by increasing the pressure. Around a pressure of 160 bar, the crossover region was observed for dyes. Below this region, solubility increases with decreasing temperature, and above 160 bar, the solubility increases by increasing temperature.

Application of Chrastil's density-based model to the experimental data leads to values of k = (1.8, 28.1, and 6.2), a = (−3202, −28155, and −9833) K, b = (−20.2, −206.6, and −43.3), and ΔH = (−29.04, −225.3, and −82.2) kJ·mol^{-1} for Dye 1, Dye 2, and Dye 3, respectively. These data were correlated with an overall AARD of 18.6 % for three dyes.

The solubility results obtained in this work are very promising for the development of supercritical processes for dyeing applications based on these disperse dyes.

Literature Cited

(1) Guzel, B.; Akgerman, A. Mordant Dyeing of Wool by Supercritical Processing. *J. Supercrit. Fluids* **2000**, *18*, 247–252.
(2) Beltrame, P. L.; Castelli, A.; Selli, E.; Mossa, A.; Testa, G.; Bonfatti, A. M.; Seves, A. Dyeing of Cotton in Supercritical Carbon Dioxide. *Dyes Pigments* **1998**, *39*, 335–340.
(3) Park, M. W.; Bae, H. K. Dye Distribution in Supercritical Dyeing with Carbon Dioxide. *J. Supercrit. Fluids* **2002**, *22*, 65–73.
(4) Chafer, A.; Fornari, T.; Stateva, R. P.; Berna, A. D-Pinitol Solubility in Supercritical CO_2: Experimental Data and Correlation. *J. Chem. Eng. Data* **2006**, *51*, 612–615.
(5) Ozcan, A.; Ozcan, A. S. Solubility of an Acid Dye in Supercritical Carbon Dioxide by Ion-Pairing with Dodecyltrimethylammonium Bromide. *Fluid Phase Equilib.* **2006**, *249*, 1–5.

(6) Cabral, V. F.; Santos, W. L. F.; Muniz, E. C.; Rubira, A. F.; Cardozo-Filho, L. Correlation of Dye Solubility in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **2007**, *40*, 163–169.

(7) Coimbra, P.; Gil, M. H.; Duarte, C. M. M.; Heron, B. M.; de Sousa, H. C. Solubility of a Spiroindolinonaphthoxazine Photochromic Dye in Supercritical Carbon Dioxide: Experimental Determination and Correlation. *Fluid Phase Equilib.* **2005**, *238*, 120–128.

(8) Knittel, W.; Schollmeyer, E. Dyeing with Supercritical CO_2, Research with Different Types of Dyes. *Melliand Textilber* **1995**, *76*, 1092–96.

(9) Bach, E.; Cleve, E.; Schollmeyer, E. Dyeing of Polyethyleneterephthalate Fibers in Supercritical Carbon Dioxide. In *Process Technology Proceeding, No. 12, High-pressure Chemical Engineering*; Von Rohr, Ph. R., Trepp, Ch., Eds.; Elsevier Science: Amsterdam, 1996; pp 581–586..

(10) Lee, J. W.; Park, M. W.; Bae, H. K. Measurement and Correlation of Dye Solubility in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **2001**, *179*, 387–394.

(11) Tamura, K.; Shinoda, T. Binary and Ternary Solubilities of Disperse Dyes and Their Blend 13 in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **2004**, *219*, 25–32.

(12) Huang, Z.; Kawi, S.; Chiew, Y. C. Application of the Perturbed Lennard-Jones Chain Equation of State to Solute Solubility in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **2004**, *216*, 111–122.

(13) Mishima, K.; Matsuyama, K.; Ishikawa, H.; Hayashi, K.; Mae, S. Measurement and Correlation of Solubilities of Azo Dyes and Anthraquinone in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **2002**, *194–197*, 895–904.

(14) Tamura, K.; Shinoda, T. Binary and Ternary Solubilities of Disperse Dyes and Their Blend in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **2004**, *219*, 25–32.

(15) Joung, S. N.; Shin, H. Y.; Park, Y. H.; Yoo, K. Measurement and Correlation of Solubility of Disperse Anthraquinone and Azo Dyes in Supercritical Carbon Dioxide. *Korean Chem. Eng.* **1998**, *15*, 78–84.

(16) Gordillo, M. D.; Pereyra, C.; Martínez de la Ossa, E. J. Solubility Estimations for Disperse Blue 14 in Supercritical Carbon Dioxide. *Dyes Pigments* **2005**, *67*, 167–173.

(17) Gharanjig, K.; Arami, M.; Bahrami, H.; Movassagh, B.; Mohmoodi, N. M.; Rouhani, S. Synthesis, spectral properties and application of novel monoazo disperse dyes derived from N-ester-1,8-naphthaimide to polyester. *Dyes Pigments* **2008**, *76*, 684–689.

(18) Gharanjig, K. Synthesis and investigation of dyeing properties of novel dispers dyes with hydrolysable properties in alkali media. Ph.D Thesis, Amir Kabir University of Technology, Tehran, Iran, 2007, p 62.

(19) Khosravi, A.; Moradian, S.; Gharanjig, K.; Afshar Taromi, F. Synthesis and spectroscopic studies of some naphthalimide based disperse azo dyestuffs for the dyeing of polyester fibres. *Dyes Pigments* **2006**, *69*, 79–92.

(20) Yamini, Y.; Fat'hi, M. R.; Alizadeh, N.; Shamsipur, M. Solubility of Dihydroxybenzene Isomers in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1998**, *152*, 299–305.

(21) Swidersky, P.; Tuma, G. M.; Schneider, G. M. High-Pressure Investigation on the Solubility of Anthraquinone Dyestuffs in Supercritical Gases by VIS/NIR Spectroscopy. Part II. *J. Supercrit. Fluids* **1996**, *9*, 12–8.

(22) Koga, Y.; Iwai, Y.; Arai, Y. Monte Carlo Simulation for Chain Molecules in Supercritical Ethane. *J. Chem. Phys.* **1994**, *101*, 2283–88.

(23) Draper, S. L.; Montero, G. A.; Smith, B.; Beck, K. Solubility Relations for Disperse Dyes in Supercritical Carbon Dioxide. *Dyes Pigments* **2000**, *45*, 177–83.

(24) Foster, N. R.; Gurdial, G. S.; Yun, J. S. L.; Liong, K. K.; Tilly, K. D.; Ting, S. S. T.; Singh, H.; Lee, J. H. Significance of the Crossover Pressure in Solid-Supercritical Fluid Phase Equilibria. *Ind. Eng. Chem. Res.* **1991**, *30*, 1955–64.

(25) Fasihi, J.; Yamini, Y.; Nourmohammadian, F.; Bahramifar, N. Investigations on the Solubilities of Some Disperse Azo Dyes in Supercritical Carbon Dioxide. *Dyes Pigments* **2004**, *63*, 161–168.

(26) Pitzer, K. S. The Volumetric and Thermodynamic Properties of Fluids. I. 455 Theoretical Basis and Virial Coefficients. *J. Am. Chem. Soc.* **1955**, *77*, 3427–33.

(27) Pitzer, K. S.; Lippman, D. Z.; Huggins, C. M.; Petersen, D. E. I. The volumetric 457 and Thermodynamic Properties of Fluids. II. Compressibility Factor, Vapor 458 Pressure and Entropy of Vaporization. *J. Am. Chem. Soc.* **1955**, *77*, 3433–40.

(28) Brunner, G. Selectivity of Supercritical Compounds and Entrainers with Respect to Model Substances. *Fluid Phase Equilib.* **1983**, *10*, 289–298.

(29) Jouyban, A.; Chan, H. K.; Foster, N. R. Mathematical Representation of Solute Solubility in Supercritical Carbon Dioxide Using Empirical Expressions. *J. Supercrit. Fluids* **2002**, *24*, 19–35.

(30) Garnier, S.; Neau, E.; Alessi, P.; Cortesi, A.; Kikic, I. Modeling Solubility of Solids in Supercritical Fluids Using Fusion Properties. *Fluid Phase Equilib.* **1999**, *158–160*, 491–500.

(31) Xu, G.; Scurto, A. M.; Castier, M.; Brennecke, J. F.; Stadtherr, M. A. Reliable Computation of High-Pressure Solid Fluid Equilibrium. *Ind. Eng. Chem. Res.* **2000**, *39*, 1624–1636.

(32) Chrastil, F. J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016–21.

Received for review June 25, 2007. Accepted January 10, 2008.

JE7003534