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J. of Supercritical Fluids 27 (2003) 31–37

THE JOURNAL OF Supercritical Fluids

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Measurement and correlation of solubility of Disperse Blue 14 in supercritical carbon dioxide

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Received 17 June 2002; received in revised form 16 August 2002; accepted 5 September 2002

Abstract

The solubility of solid 1,4-dimethylaminoanthraquinone (Disperse Blue 14) in supercritical carbon dioxide has been determined in the pressure range of 100–350 bar and in the temperature range of 313–353 K. The values obtained have been correlated with two types of model: the first is based on empirical and semiempirical equations and the second is based on thermodynamic aspects and the use of equations of state, namely Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations. The thermodynamic model, based on fitting the solid sublimation pressure and binary interaction parameter, shows better agreement with the experimental data than the empirical and semiempirical equations.

Keywords: Solubility; Supercritical; Correlation; Carbon dioxide; Disperse dyes

1. Introduction

In the textile industry, one of the most important classes of compound for the dyeing of synthetic fibers is represented by the anthraquinone disperse dyes. Among these compounds, 1,4-dimethylaminoanthraquinone (Disperse Blue 14) is one of the most widely used. The conventional dyeing process consists of numerous stages during which, several auxiliary compounds must be added to overcome the hydrophobicity of this class of dye. On completion of the dyeing process, cleaning and drying of fiber is undertaken.

The large quantity of water used during the dyeing process results in a large volume of wastewater that contains not only all of the auxiliary agents but also a great remains of the dye.

The use of the supercritical dyeing technique circumvents the needs for water and wastewater treatment in the dyeing process. In addition, the fibers that are dyed in the supercritical fluid are completely dry after reducing the pressure to atmospheric conditions, thus precluding the requirement of drying step associated [1].

Supercritical dyeing requires studies of phase equilibrium between dyes and the supercritical solvent. For this reason, we have undertaken a

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PII: S0896-8446(02)00215-2

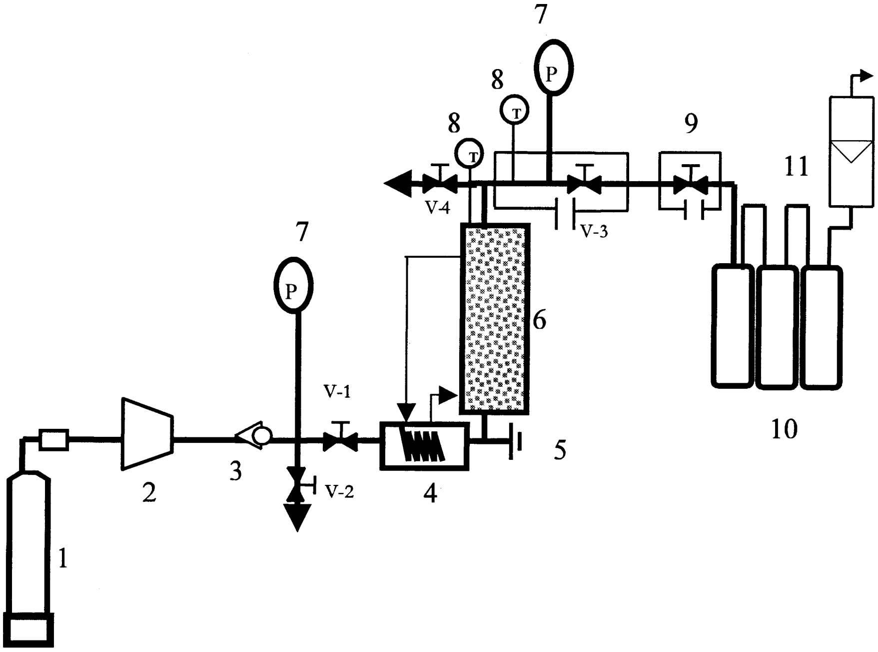

Fig. 1. Schematic flow diagram of the experimental apparatus. (1) Gas tank, (2) compressor, (3) check valve, (4) constant temperature bath with preheater, (5) rupture disc, (6) equilibrium cell, (7) pressure gauge, (8) thermocouple, (9) metering valve, (10) cold traps, (11) volumetric flow meter.

study of the CO_2/Disperse Blue 14 equilibrium at different pressures and temperatures.

2. Experimental

The apparatus used in this study was especially designed in our laboratories in order to measure solubility. The flow diagram of the installation is shown in Fig. 1, and the equipment and its main operating steps are described below.

The gaseous solvent, carbon dioxide, was introduced into a Nova Swiss compressor capable of providing a maximum pressure of 1600 bar. The CO_2 was delivered by the compressor through a heating coil so that the CO_2 could attain the desired operating temperature prior to entering the equilibrium cell.

The equilibrium cell was constructed from stainless steel tubing (42 cm long and an ID of 0.88 cm). The cell was packed with alternate layers of the dye and glass beads and was surrounded by a heating jacket through which hot water was passed in order to achieve the appropriate process temperature. Flow control was maintained with a flow-metering valve. The dye that was dissolved in supercritical CO_2 was separated from the carbon dioxide and collected in three cold traps containing

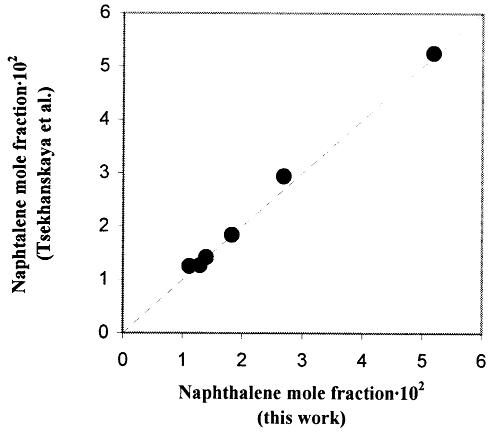

Fig. 2. Solubility of naphthalene in supercritical carbon dioxide: values obtained by Tsekhanskaya et al., vs. values obtained in this work.

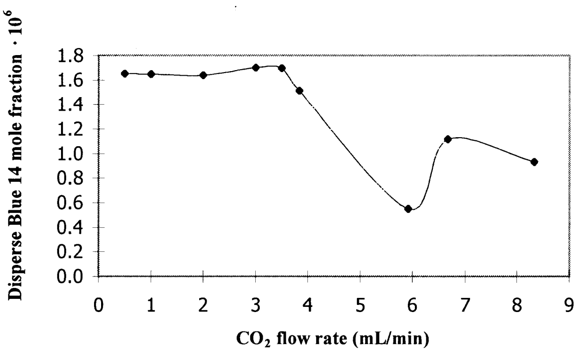

Fig. 3. Effect of carbon dioxide flow rate on the solubility determination.

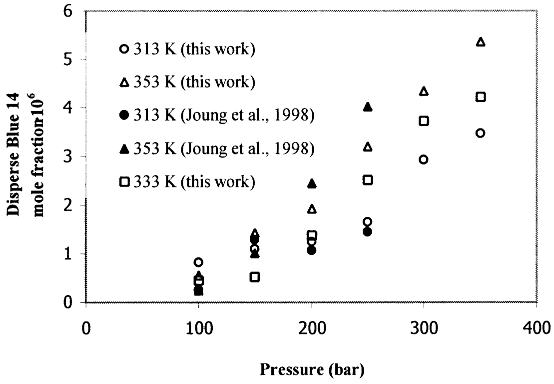

Fig. 4. Experimental solubility of Disperse Blue 14 in supercritical carbon dioxide.

acetone. The CO_2 then passed through a flow meter of Hastings Instruments.

A UV–visible spectrophotometer Shimadzu (Multipurpose Recording Spectrophotometer MPS-2000) was used to analyze the dye per acetone samples. It showed a sharp absorption maximum at 641 nm.

Disperse Blue 14 was supplied by Aldrich (minimum purity of 97%) and the carbon dioxide was supplied by Carburos Metálicos, S.A. with a minimum purity of 99%.

The validity of the experimental technique was first determined by measuring the solubility of naphthalene in supercritical carbon dioxide at 120 and 300 bar and 308, 318 and 328 K. The data are comparable to those reported by Tsekhanskaya et al. [2] (Fig. 2).

To check that the solvent flow was the adequate one to keep the CO_2 saturated in Disperse Blue 14, the flow range where the solubility does not change was determined. At 250 bar and 313 K, Fig. 3 shows this effect.

As can be seen, the solubility of Disperse Blue 14 does not change at a range among 0.5–3.5 ml/min. Above this range it is not possible to operate because the system can not reach the equilibrium; below 0.5 ml/min is not possible either because it would imply a difficult quantification of the total amount of solvent. Therefore, the flow rate was controlled within the range of 0.5–3.5 ml (STP)/min.

3. Results and discussion

3.1. Experimental solubility data

Experimental solubility data as mole fraction for Disperse Blue 14 (266.3 g/mol) in supercritical carbon dioxide at 313, 333 and 353 K and 100–350 bar are shown in Fig. 4. The reproducibility of each determination is 1.0×10^{-7} mol fraction. From the obtained results it can be seen that Disperse Blue 14 solubility always increases as the pressure does. The solubility behavior with temperature is more complex. At pressures of 100 and 150 bar, the solubility behavior with temperature is not clear. For pressures above 150 bar, the solubility increases with increasing temperature.

This solubility trend is consistent with those observed by different authors for different dyes [3–5]. Joung et al. [3] measured the solubility of the same dye. The data reported by the aforementioned authors are also shown in Fig. 4. The values of solubility obtained at 313 K are very similar to those obtained by Joung et al. It can be observed that the data obtained in this work at 353 K for pressures above 200 bar are smaller that were reported by Joung et al., and higher for pressures of 100 and 150 bar.

Table 1
Calculated regression parameters and deviations for Eqs. (1)–(4)

Equation 1	
c_0	-0.5360
c_1	-3140.0
c_2	1.9402
R^2	0.8191
AARD (%)	27.41
Equation 2	
c_0	44.68
c_1	$-33\,251$
c_{11}	5×10^6
c_2	1.9309
R^2	0.8295
AARD (%)	27.49
Equation 3	
b_0	5.46×10^{-5}
b_1	-5.95×10^{-8}
b_{11}	2.65×10^{-11}
b_2	-3.12×10^{-7}
b_{22}	4.40×10^{-10}
b_{12}	1.91×10^{-10}
R^2	0.9779
AARD (%)	14.33
Equation 4	
a_0	-13.35
a_1	9.34×10^{-3}
a_2	-7.21×10^{-2}
a_3	6.84×10^{-5}
a_4	-1.16×10^{-5}
a_5	-5.35×10^{-4}
R^2	0.9363
AARD (%)	15.42

3.2. Empirical and semiempirical data correlation

Several semiempirical models have been described in the literature and two of these were selected to relate the solubility with the temperature and the density of the solvent: the Chrastil [6] and Del Valle and Aguilera [7] equations (Eqs. (1) and (2), respectively):

$$\ln c = c_0 + \frac{c_1}{T} + c_2 \ln \rho \tag{1}$$

$$\ln c = c_0 + \frac{c_1}{T} + \frac{c_{11}}{T^2} + c_2 \ln \rho \tag{2}$$

In both of these equations c is the solubility of the solid expressed in g/l, T is the temperature in K, ρ is the density of the solvent in g/ml and the fitting parameter are represented by c_i and c_{ii}.

The third equation that was employed in this study was that developed by Yu et al. [8], whose development is completely empirical and which relates the solubility (y, expressed as mole fraction) with pressure (bar) and temperature (K):

$$y = b_0 + b_1 P + b_{11} P^2 + b_2 T + b_{22} T^2 + b_{12} PT(1-y) \tag{3}$$

The last of the empirical equations used was developed in one of our previous studies [9] and is derived from the equation shown above:

$$\ln y = a_0 + a_1 P + a_2 T + a_3 PT + a_4 P^2 + a_5 T^2 \tag{4}$$

where y is the solid mole fraction in the solvent, P the pressure in bar, T the temperature in °C and a_i are the fitting parameters.

The results obtained on using the four equations are presented in Table 1. The errors in the fitting were determined by calculating the average absolute relative deviation (AARD) between the measured and calculated data. AARD is defined as:

$$\text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}} \right| 100 \tag{5}$$

The experimental results are shown in Fig. 5 along with those obtained with the empirical and semiempirical equations.

For equations that depend on the density of the solvent, AARD values in the order of 27% are obtained. The introduction of a new fitting parameter to the equation of Chrastil, that is to say, the equation of Del Valle and Aguilera, doesn't improve the correlation of the experimental data.

For equations that depend on the operation pressure and temperature, values in the order of 15% are obtained. However, in any case, it can be seen from Fig. 5 that the calculated trends do not coincide with the experimental data obtained.

3.3. Thermodynamic modeling

The mole fraction of Disperse Blue 14 in the supercritical fluid (y_2) was calculated from its thermodynamic definition [10]:

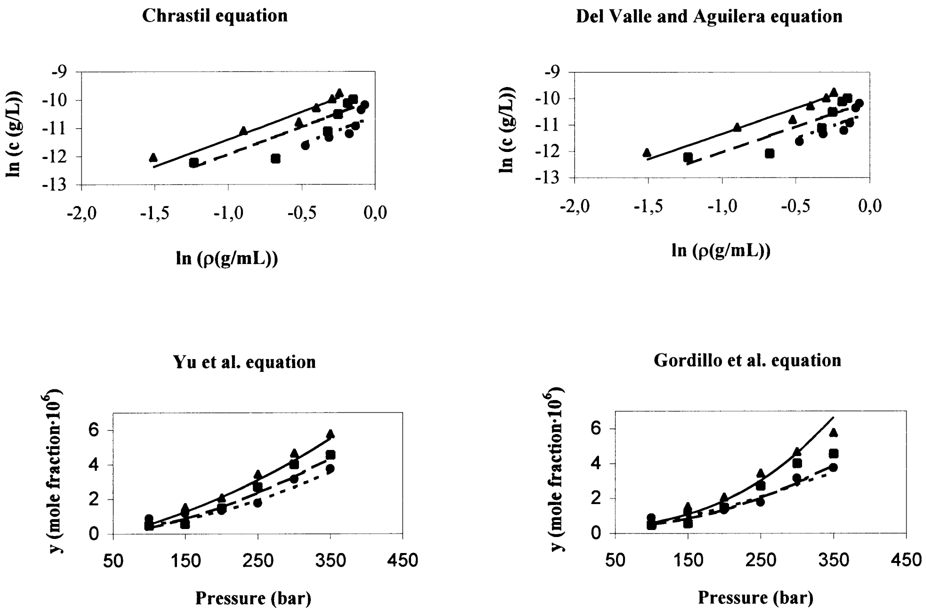

Fig. 5. Solubility of Disperse Blue 14 in supercritical carbon dioxide. ●, ■, ▲, ······, – – –, —: Experimental results and results obtained by empirical and semiempirical equations at 313, 333 and 353 K, respectively.

Table 2
Thermodynamic modeling results

T (K)	RK			SRK			PR		
	K_{12}	AARD (%)	P_2^{sat} (bar)	K_{12}	AARD (%)	P_2^{sat} (bar)	K_{12}	AARD (%)	P_2^{sat} (bar)
313	−0.105	29.19	1.3×10^{-13}	−0.381	30.47	1.0×10^{-12}	−0.772	28.76	1.0×10^{-12}
333	−0.022	20.62	7.9×10^{-11}	−0.214	22.04	2.0×10^{-10}	−0.478	20.80	4.0×10^{-10}
353	−0.006	35.70	1.0×10^{-9}	−0.079	28.59	1.0×10^{-8}	−0.254	27.94	2.5×10^{-8}
AARD ($350\geq P\geq 100$; %)		28.53			28.59			25.83	
AARD ($P\geq 200$; %)		7.50			7.74			4.94	

T_c, 820.16 K; P_c, 24.60 bar; V_c, 794 cm^3/mol; ω, 1.141; υ_2^S, 203.6 cm^3/mol.

$$y_2=\frac{P_2^{\mathrm{sat}}}{\hat{\phi}_2^{\mathrm{F}}P}\exp\frac{(P-P_2^{\mathrm{sat}})\upsilon_2^{\mathrm{S}}}{RT} \tag{6}$$

where P_2^{sat} and υ_2^{S} are the saturation pressure (sublimation pressure in this case) and the molar volume of pure solid, respectively, and $\hat{\phi}_2^{\mathrm{F}}$ is the fugacity coefficient of the solid in the supercritical phase (at pressure P and temperature T). The calculation of the solubility y_2, therefore, requires a knowledge of P_2^{sat}, υ_2^{S} and an equation of state (with its associated mixing rules) for the calculation of $\hat{\phi}_2^{\mathrm{F}}$.

In the work described here, Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state with Lorentz–Berthelot mixing rules were used to calculate the fugacity coefficient [11]. In order to calculate this coefficient, a binary interaction parameter K_{ij} must be obtained by fitting the experimental solubility data. The acentric factor (ω) was calculated by the Lee–Kesler correlation [11]. The solid molar volume was estimated by the Immirzi and Perini group contribution method [12].

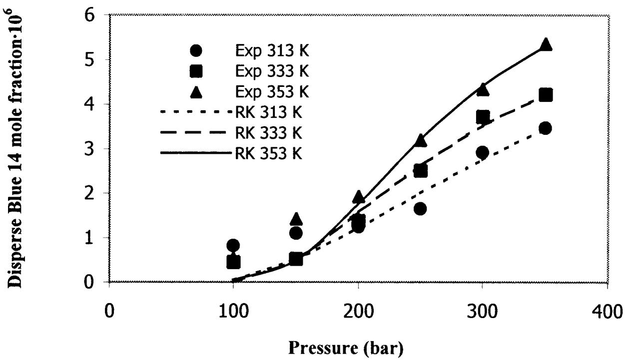

Fig. 6. Solubility of Disperse Blue 14 in supercritical carbon dioxide. ●, ■, ▲, ·····, – – –, —: Experimental results and results obtained by the thermodynamic model with RK at 313, 333 and 353 K, respectively.

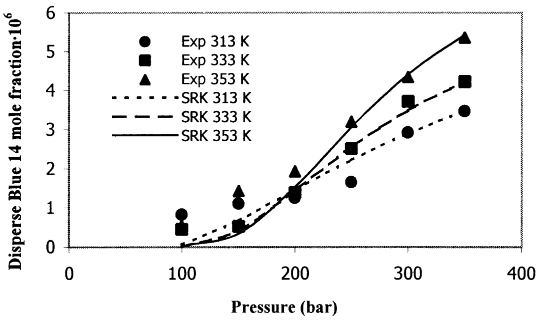

Fig. 7. Solubility of Disperse Blue 14 in supercritical carbon dioxide. ●, ■, ▲, ·····, – – –, —: Experimental results and results obtained by the thermodynamic model with SRK at 313, 333 and 353 K, respectively.

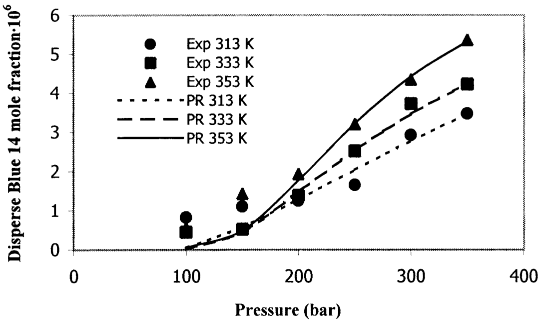

Fig. 8. Solubility of Disperse Blue 14 in supercritical carbon dioxide. ●, ■, ▲, ·····, – – –, —: Experimental results and results obtained by the thermodynamic model with PR at 313, 333 and 353 K, respectively.

Lydersen's [13] and Fedors's [14] group contribution methods were used to estimate the critical pressure, volume and temperature of Disperse Blue 14.

For this system, two parameters—the binary interaction parameter (K_{12}) and the sublimation pressure of Disperse Blue 14 (P_2^{Sat})—were fitted by minimizing the error (AARD) between experimental and calculated solubility data. If the sublimation pressure is measured or estimated and the interaction parameter is a constant independent of temperature, the use of a cubic EOS is a thermodynamically rigorous procedure. In this work, the use of this model is a empirical computational procedure. The thermodynamic modeling results are shown in Table 2: estimated properties of Disperse Blue 14, the predicted Disperse Blue 14 sublimation pressure and the binary interaction parameter obtained by regressing the experimental data with RK, SRK and PR equations of state and Lorentz–Berthelot mixing rules.

As one would expect, the values of the sublimation pressure data increase with temperature, and these values can be adjusted to the Clapeyron equation, as it will be analyzed further down. The results obtained for the prediction of solubility show that none of the models fit the solubility data appropriately for 100 and 150 bar. However, at pressures above 150 bar, in all three cases, the agreement between calculated and experimental data can be considered very good, as can be seen in Figs. 6–8. The difference between these methods, therefore, resides in the binary interaction para-

Table 3
Correlation coefficient of K_{12} with temperature and adjustment of P_2^{sat} values to the Clapeyron equation

	R^2 (K_{12} vs. T (K))	R^2 (log P_2^{sat} (bar) vs. $1/T$ (K))	A (Clapeyron)	B (Clapeyron)
RK	0.8675	0.9558	22.002	10 853
SRK	0.9963	0.9974	23.419	11 069
PR	0.9939	0.9951	26.991	12 178

meter and the sublimation pressure values obtained.

The correlation with the PR equation (AARD = 25.83 and 4.94% at pressures above 200 bar) is better than that obtained with the RK and SRK equations.

The lowest values of P_2^{sat} are obtained on using the RK equation of state. Higher values are obtained on using the SRK or PR equations but there is no discernable difference between these two methods. The K_{12} values (absolute value) increase from RK to SRK and PR and these values increase with temperature in all cases.

For equations that depend on acentric factor, i.e. SRK and PR EOS, better results are obtained in terms of correlation between the coefficient K_{12} and temperature and the adjustment of P_2^{sat} values to Clapeyon equation, as can be seen from the results in Table 3. Therefore, modeling of the carbon dioxide/Disperse Blue 14 equilibrium could be performed by using either of these two equations, since good trends and good correlation coefficients for the adjustment parameters are obtained in both cases.

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