Measurement and Correlation of Solubility of Red 153 in Supercritical Carbon Dioxide

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Solubility measurements of red 153 in supercritical carbon dioxide were carried out in a flow type apparatus, at the temperature range from 323 to 393 K and for pressures from 15 to 40 MPa. The dynamic apparatus consists of the usual three sections of compression, equilibrium and expansion but some modifications have been introduced. The supercritical fluid mixture including the dye was released at the expansion valve and the dye was trapped in a system of filters without organic solvents. The dye precipitated in the system during the depressurization was recovered by washing out with methanol and analyzed in a UV-Vis spectrophotometer. The values of solubility change from 9.35×10^{-7} to 3.71×10^{-5}. Semi empirical density-based models were used to correlate the solubility of red 153 in supercritical carbon dioxide. From the correlation results, the head of red 153-CO_2 solvation and that of solute dye vaporization were determined and compared with the results in literature.

INTRODUCTION

Supercritical dyeing technology is an innovative method to reduce waste discharge and energy consumption for the textile industry, being an innovate technology with a lot of potential advantages, especially for synthetic fibres [1,2]. The application of this process requires a study to determine the dye solubility in supercritical carbon dioxide (SC CO_2). The temperature and pressure (consequently density) of dyes solubilities in SC CO_2 must be know with precision, as well the mathematical modelling of the systems with the aim to promote the development of supercritical fluid process.
In literature some data of solubility of different dyes in SC CO_2 presented considerably differences. Results to red 153 were presented before [1], namely two isotherms at 353.2 and 393.2 K and pressures from 15 to 30 MPa. However we increase the date and the obtained values of solubility are considerably higher than that reported in the study of Lin *et all* [1]. The same fact was verified by Huang et al [3] to the dye disperse blue 79, where their values of solubility was significantly higher.
Moreover, results were modelled using four semi empirical density-based models (Chrastil model [4], Bartle model [5], M-T model [6] and K-J model [7]) and from the correlation results, the head of red 153-CO_2 solvation and that of solute dye vaporization were determined and compared with the results in literature.

MATERIALS AND METHODS

The supercritical fluid extraction experiments were performed in a flow apparatus (Figure 1). This equipment allows carrying out studies at a temperature up to 120ºC and a pressure up to 600 bar.
The liquid CO_2 flowing from the cylinder was compressed to the desire pressure (Applied Separations, Spe-ed^{TM} SFE) into the cells, which is heated. Then CO_2 comes through a bed of glass spheres, propylene wool, 5-6 g of dye, propylene wool and bed of glass spheres. The total volume of CO_2 was determined with a mass flow meter GFM and a totalizer. The CO_2 (99.995% purity) was supplied by Air Liquide (Portugal).
Conditions of solubility studies were: CO_2 flow rates of 0.310 $g.min^{-1}$ (liner velocity of 0.242 $cm.min^{-1}$), pressures up to 400 bar and temperatures up to 120 ºC. The conditions were supervised

during all experiments. The extracts were collected in a system of filters, at the atmospheric pressure and a temperature controlled with an ice bath.
The disperse dye red 153 was supplied by DyStar – Anilinas Têxteis, Unip.Lda, Portugal.

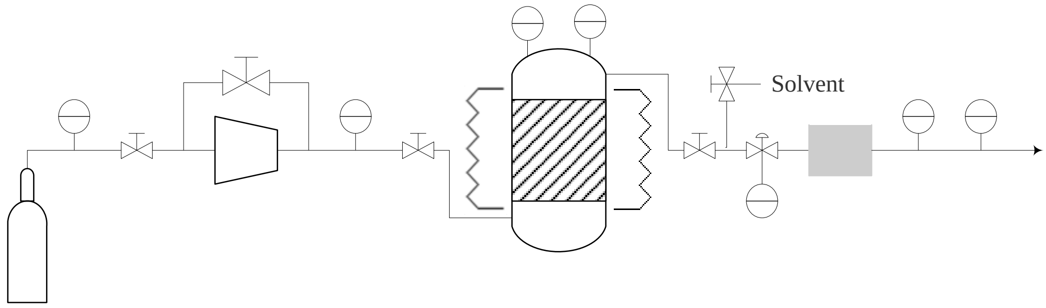

Figure 1: Diagram of the supercritical fluid extraction apparatus. CO_2; C, compressor; E, extractor; S, separator; BP, back-pressure regulator; MM, micrometer valve; MV, flow meter; Tot, totalizer; TI, temperature indicator, PT, pressure indicator.

The solubility of red 153 was determined by a spectrophotometric method (Thermo Electron Corporation, model Nicolat evolution 300LC) on the basis of the absorbance of the composition (UV) at 513 nm, being the filters washed and the solute collected in a solvent organic (methanol). Calibration was made with twelve samples over a composition range of $1.0x10^{-4}$ – $1.0x10^{-6}$ mol/L. Three replicates were performance at each experimental conditions and the solubility was obtained by an average of these results. The uncertainty of the solubility measurements was 8 %.

RESULTS AND CONCLUSIONS

The experimental results of solubility of red 153 in SC CO_2, are showed is figure 2 and figure 3. Our results are about 60 % higher than that ones presented by Lin *et all* [1]. Fig.2 shows the equilibrium solubility of disperse red 153 in supercritical carbon dioxide as function of the pressure and to different temperatures. When the pressure increase at constant temperature, the mole fractions increases due to increasing in the fluid density.

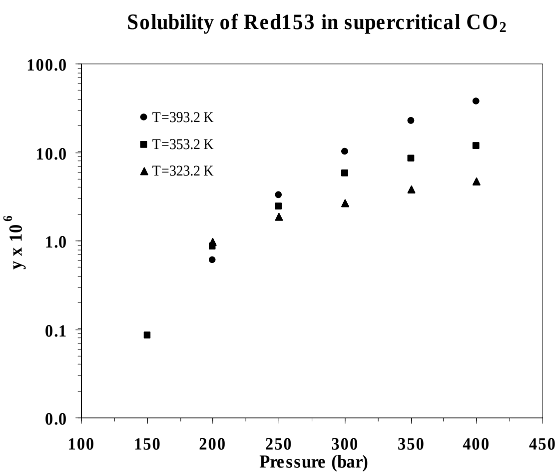

Figure 2: Solubility of red 153 in SC CO_2 as a function of pressure.

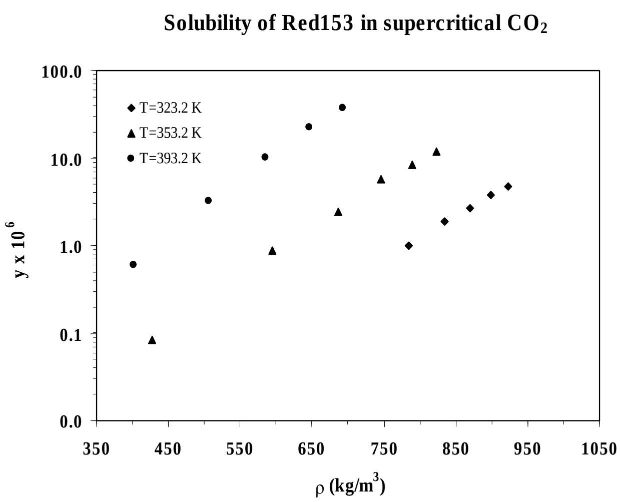

Figure 3: Solubility of red 153 in SC CO_2 as a function of density.

However, solubility curves of the dye intersect at each other around 200–250 bar. This can be explained by the following effects. At constant pressure, the solubilities of dye decreases as the density of carbon dioxide decreases with increasing temperature. In another way, at constant pressure, the solubility of dye increases with increasing temperature because of a rising diffusion power of the solute and respectively vapour pressure. That last effect can be better presented in Fig.3.

Semi empirical density-based models are applied to correlate the solubility of the dye in supercritical carbon dioxide. The equations are presented in Table 1. The discussion and analysis to different data of dyes of the equations have been presented by Huang *et all* [3].

Table 1: Semi empirical density-based by calculating the red 153 solubility in supercritical CO_2

Josef Chrastil, Eq.[4]	$\ln y = a_0 + a_1 \ln \rho + \frac{a_2}{T}$	$\Delta H_{total} = -a_2 . R$
Kumar and Johnston, Eq.[5]	$\ln y = b_0 + b_1 \rho + \frac{b_2}{T}$	$\Delta H_{total} = -b_2 . R$
Bartle *et all.*, Eq.[6]	$\ln \frac{y.P}{P_{ref}} = c_0 + c_1(\rho - \rho_{ref}) + \frac{c_2}{T}$	$\Delta H_{vap} = -c_2 . R$
Méndez–Santiago and Teja, Eq.[7]	$T . \ln(y.P) = d_0 + d_1 . \rho + d_2 . T$	

A comparison among the four models reveals that the Bartle's model gives better correlations to the solubility data than, the others three models, with an overall average absolute relative deviation in the mole fraction (AARD) of 8.1%. Figure 4, show the results obtained to the correlation of Bartle [5].

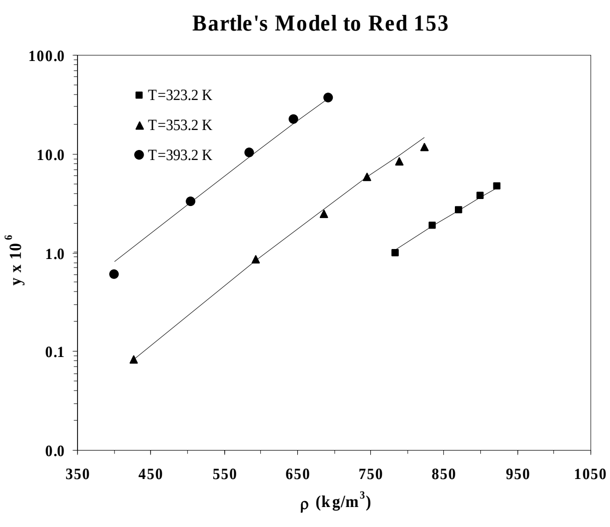

Figure 4: Solubility of red 153 in SC CO_2 as a function of density and results for the Bartle's model.

The parameter $\boldsymbol{c_2}$, is related to the enthalpy of vaporization of the solid state ΔH_{vap}, where R is the gas constant. The estimated value to our results is 85.22 kJ/mol. Using the total enthalpy of the process, estimated by the Chrastil model [4] and K-J model [7] (71.50 kJ/mol), it is possible to estimate the enthalpy of red 153-CO_2 solvation, 13.72 kJ/mol.
Despite ours experimental solubility of red 153 are significantly higher than that one presented by Lin *et all* [1], when compared the enthalpies obtained with the correlations applied by Huang *et all* [3], the results are quite similar, with a maximum deviations of 3%.

The results show that these models could be applied for a satisfactory solubility prediction in that case. From the correlation results, the enthalpy of red 153-CO_2 solvation and that of solute dye vaporization were determined.

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