

ON-LINE CONTROL OF A RED AZO DISPERSE DYE : VIS ABSORPTION SPECTROPHOTOMETRY WITH SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Azo disperse dyes should be used in supercritical carbon dioxide for dyeing polyesters fibres. We have focused this study on one pure dye, prepared by CIBA: red SM1P. The solubility measurements for practical applications were carried out in two static stirred high pressure cells : a thermostat high pressure view cell by visual inspection of the phases (P max =75 MPa, T max = 150°C) and an other cell (P max =75 MPa, T max = 250 °C) equipped with two sapphire windows was used for UV-vis spectrophotometer measurements.

Extraction of red SM1P with supercritical carbon dioxide was investigated at 80°C and 20MPa over a wide range of contact times on a laboratory equipment, modified with on-line UV-visible spectrophotometer detector, at the outlet of the extraction column.

INTRODUCTION

Solubility data of dispersion dyestuffs in supercritical fluids are needed for development of supercritical dyeing processes. Unfortunately, the available data are rather limited in the public literature. Here we propose to compare three experimental methods to determine solubility of Red SM1P. Dynamic extraction is proposed in order to study the dissolution kinetics and also an on line spectroscopic measurement in order to apply it on a pilot plant apparatus.

MATERIALS AND METHODS

Chemicals

The used colouring agents are products which are supplied to us by the company CIBA, conceived specially for dyeing fibres in supercritical CO₂, which appear under the following formulae (Figure 1).

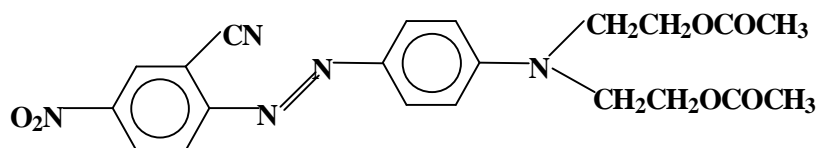


Figure 1. Red SM1P(CI disperse RED 82 (IC 11140) Red Terasil 3BL)

Experimental equipment

One window cell

The measures of solubility are realised by using two high pressure cells. The first is based on the observation of the phenomena of equilibrium phases. It contains an autoclave with variable volume, which is adjusted by manual compression by means of a piston. The volume

varies from 12 to 1.7 cm³. The homogeneity of the mixture (colouring +CO₂) is made by stirring. The visualisation is done through a sapphire window , by a camera, which is connected to a television. The maximal temperature is of 150°C, it is adjusted by a thermostat bath and the maximal pressure is of 700 Bar, it is given by a sensor of pressure. By this installation, we have to try to know the point of transition, which is the passage of a mixture of two phases: (supercritical + solid) to a homogeneous single phase mixture according to the temperature and the pressure. The plan of this cell is presented on figure2.

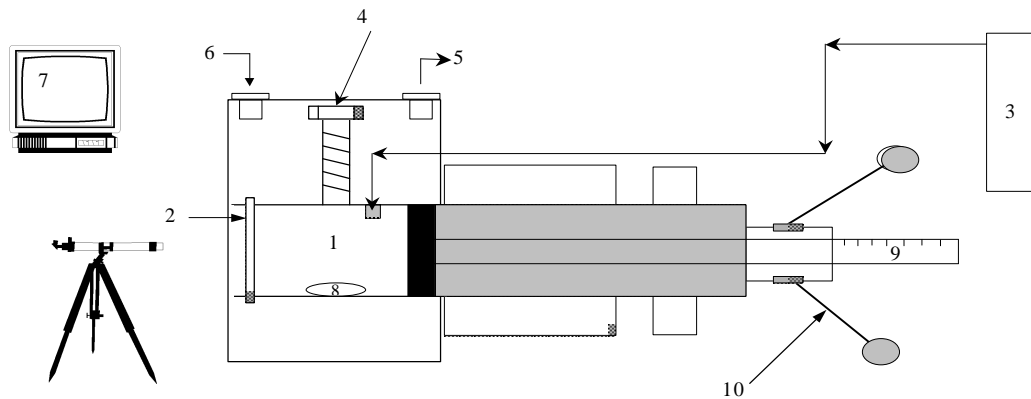


Figure 2 . Plan of one window cell. (Top Industrie).

(1)Cell ; (2) sapphire window ; (3) CO₂'s bottle ; (4) cork ; (5) circuit of water going towards thermostat bath ; (6) circuit of water resulting from thermostat bath ; (7) monitor connected to the camera ; (8) magnetised bar ; (9) gradual piston ; (10) handles of the piston.

Two windows Cell

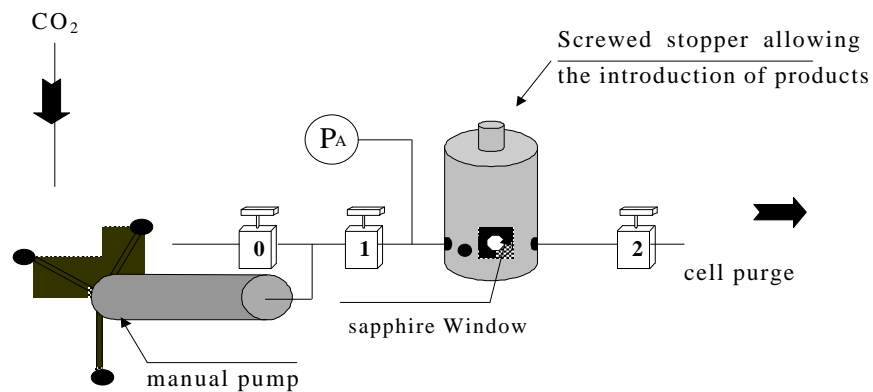


Figure 3 . Plan of the two windows cell. (Top Industrie)

The principle of this cell is to manage to measure solubility of every colouring agent by spectroscopic method. The cell is cylindrical, with an autoclave of dimensions : 65 mm in height and 14 mm of diameter which is the optical step. Its volume is of 10 cm³. The filling of the cell is done in T=5°C and P=50 bar, which is the pressure of the CO₂ bottle. The maximal temperature is of 250°C and pressure of 750 bars. It is bound to a visible spectrophotometer UV HP 8453 which allows us to make calibration curve of the colouring agent in organic

solvents and in CO₂ by changing conditions of temperature and pressure. The contents of the cell are homogenised by magnetic excitement. The equilibration time of the system is 30 min. The plan of this cell is presented on figure 3 .

Dynamic extraction

Gas CO₂ was liquefied, then it passes by a metal diaphragm pump that regulates the flow (Dosapro Milton Roy-MilRoyal D, maximum flow-rate 3.2 Kg.s⁻¹). After it is heated and CO₂ is ready to enter in the extractor vessel under supercritical phase (P = 20 MPa, T = 80°C). The CO₂ flow is measured at the inlet column with a flow-meter (Micro Motion).

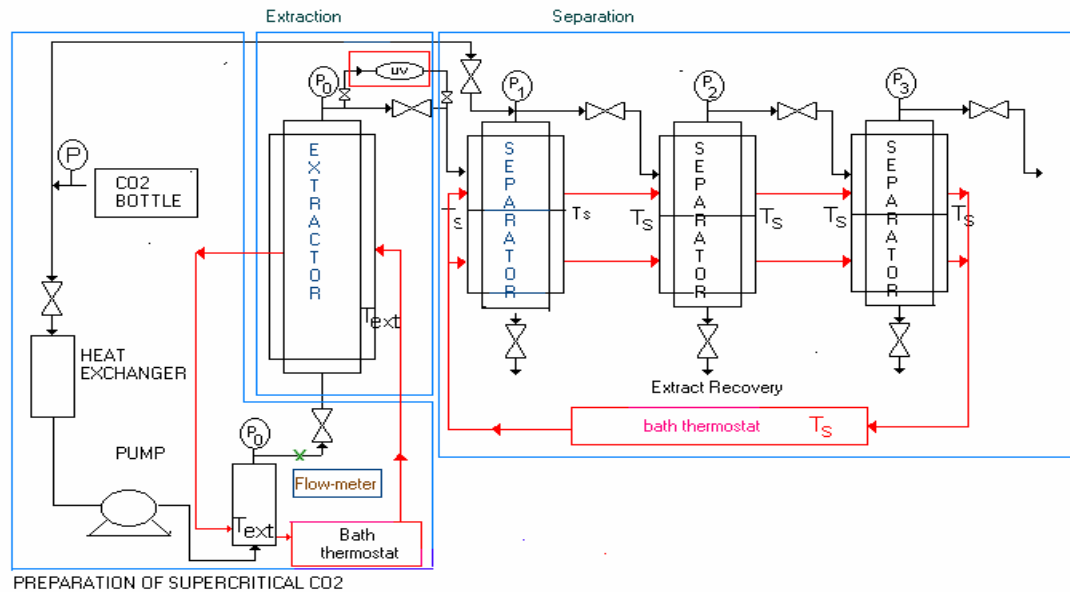


Figure 4. Dynamic extraction apparatus

The extractor vessel is a cylinder (height: 300 mm; internal diameter: 23 mm) which contains a cylindrical column. The temperature of the column is maintained thanks to a coolant circulating in a double envelope. At the outlet of the extractor, the mixture CO₂-solute is expanded through valves and is separated in three cyclonic separators [1]. These temperatures are also maintained thanks to a double envelope.

All the experiments were carried out under the same separators temperature (328 K) and pressure (20.0, 9.0 and 1.5 to 2.0 MPa for the first, second and third separator, respectively) . The dye is blended with glass beads and then packed into the extractor. A glass wool plug is placed at the bottom and at the top of the extractor to prevent entrainment of solute. The quantity of dye soluble is the difference between the feed and the refined mass weighted : the mass feed is near 2g. for all the experiments. A UV-visible spectrophotometer detector(LC 75, Perkin Elmer), at the outlet of the extraction column permit us to follow the variation of the absorbance versus time (more exactly a signal proportional to absorbance), during the extraction experiment at $\lambda_{\max} = 462$ nm.

RESULTS

1.Measures of solubility

1.1 Static Methods

1.1.1 One Window cell

We have to introduce decreasing mass of dye inside the cell in order to observe the total dissolution of the solid (70 mg to 3.6 mg.). We observed the presence of both phases:

colouring agent (solid) and CO₂ (liquid) in the initial conditions of cell filling (P= 50 bar, T = 5°C). Then a decrease of the mass of the solid during the change of experimental conditions (T, P) and a colouring of the supercritical CO₂. We were able to observe a single phase system for the Red colouring agent SM1P(m = 3.6 mg) from T=90°C and P=328 bars, who corresponds to a density of 0.7302 g/cm³ of the CO₂, and a molar fraction of 3.23*10⁻⁵ of the colouring agent.(table 1)

Apparatus	T(°C)	P(bar)	ρ CO ₂ (g/cm ³)	Solubility (g/l)*	Solubility (mol/l)*	Molar fraction (y*)
One window cell	90	328	0.730	0.29	6.61*10 ⁻⁴	3.23*10 ⁻⁵
Two windows cell**	90	273	0.666	0.03	6.8*10 ⁻⁵	4.5 * 10 ⁻⁶
Dynamic extraction	80	200	0.559	0.15	3.4*10 ⁻⁴	2.7 * 10 ⁻⁵

Table 1. Solubility of Red colouring agent SM1P in supercritical CO₂

*1 : litres of liquid CO₂ (P = 50 bar, T= 5°C)

** : near solubility

1.1.2Two windows cell

In the cell with two windows, we introduce different quantities of dye to know its values of absorbance in UV-visible between 190 and 1100 nm. according to the temperature and the pressure(m = 16.1 mg. to 0.3 mg.). To realise these spectra, we take two spectra before making our measure, the first one to eliminate the effect of the sapphire and some stainless steel; the spectra is taken with the empty cell and the second to eliminate the effect of the solvent (CO₂) that means with the cell full of CO₂. Every time, we deduce these two spectra of the measure.

The principle of this method, is to obtain the calibration curves of the colouring agent in the supercritical CO₂, so to know their solubility according to the parameters (T, P).

The measures realised with Red SM1P, have us allows to know that this colouring agent has a big absorbance in UV-visible, in λ_{max} = 460 nm.(λ_{max} = 512 nm. in acetone).An example of spectra is published [2]. We are able to present the variation of the absorbance according to the density of CO₂ for a mass m = 0.3 mg of Red SM1P [2] and to obtain a value near solubility (table 1). The obtained curve is in accordance with literature data[3]. It was not possible for higher mass to measure a solubility because the absorbance signal was too high (near or higher than saturation).

1.2Dynamic extraction

The experimental results can be separated in two major portions :

- the measurement of dye concentrations in supercritical carbon dioxide at various contact time,
- determination of equilibrium solubilities.

The definition [4] of contact time τ is given by :

$$\tau = m / F \quad (1)$$

where m (g.) refers to the weight of dye packed in the extractor and F (g./s.) represents the mass flow rate of carbon dioxide.(table 2).

m (g.)	Δm (g.)	F (g./s.)	τ (s.)	y (10^{-6})
2.1571	0.0927	0.0638	33.78	9.678
1.9927	0.1773	0.3009	6.62	3.265
2.1214	0.2178	0.1285	7.71	3.996
2.1611	0.1862	0.1907	11.33	6.115
2.1187	0.2061	0.2037	10.40	4.812
2.1173	0.1854	0.2104	10.06	5.595
2.2092	0.1898	0.2212	9.98	4.770
2.1397	0.1807	0.2485	8.61	4.487
2.1800	0.1487	0.2329	9.36	4.432
0.4778	0.1658	0.2199	2.17	4.277
0.2165	0.1353	0.2039	1.06	3.569
2.0802	0.0372	0.0067	306.66	30.067
2.0419	0.0259	0.0058	347.52	19.815
2.1855	0.0210	0.0065	336.63	11.959
2.2775	0.0557	0.0085	266.76	29.537
2.1273	0.0615	0.0113	187.36	24.557
2.2403	0.0643	0.0109	204.91	27.658
2.2250	0.0641	0.0098	226.68	30.020
2.4272	0.0542	0.0081	299.30	29.847
2.3772	0.0280	0.0039	600.56	25.512
2.1435	0.0312	0.0041	524.43	27.919
2.2908	0.0340	0.0058	389.61	22.419

Table 2 . Dynamic extraction results

Δm : mass of dye dissolved in supercritical carbon dioxide

y : molar fraction of dye in supercritical carbon dioxide

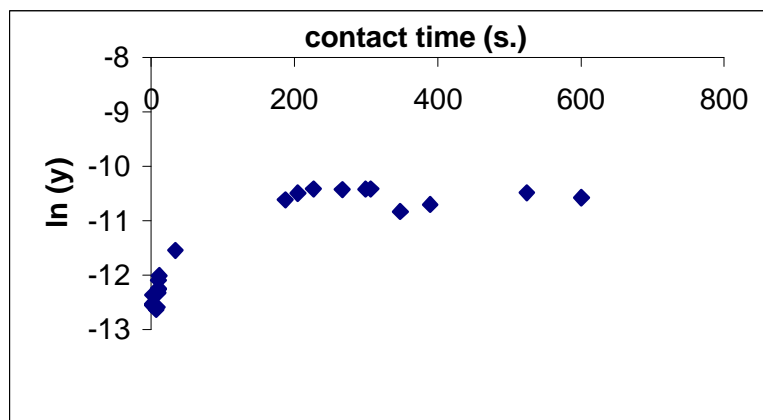


Figure 5. Concentrations of red dye in supercritical carbon dioxide at different contact time
P = 20 MPa, T = 80°C

Figure 5 illustrates the variations of dye concentration with contact time for red dye. It shows that the equilibrium conditions may be reached for long contact times. At $P = 200$ bar and $T = 80^\circ\text{C}$, the solubility y^* is $2.7 \cdot 10^{-5}$ (table 1).

Under a diffusion-controlled assumption [4], the dissolution rate of solid dyestuffs in supercritical carbon dioxide can be represented by the following equation :

$$dy / d\tau = k_0 (y^* - y) \quad (2)$$

Variable k_0 in the above equation is an effective transfer coefficient, which depends on several key factors such as the binary diffusion coefficient of the solute in the solvent, the geometry of the solid, and operating conditions. Integration of Eq. 2 and fitting the experimental values give a value of k_0 , $4.3 \cdot 10^{-3}$.

2. On-line vis absorption spectrophotometry

At the outlet of the extraction column, a part of CO_2 flow-rate cross the high pressure cell of an UV-visible spectrophotometer detector. The signal is recorded continuously as we can see on figure 6. We observe the increase of absorbance or concentration and after a certain time a stabilisation of the signal in order to reach equilibrium condition.

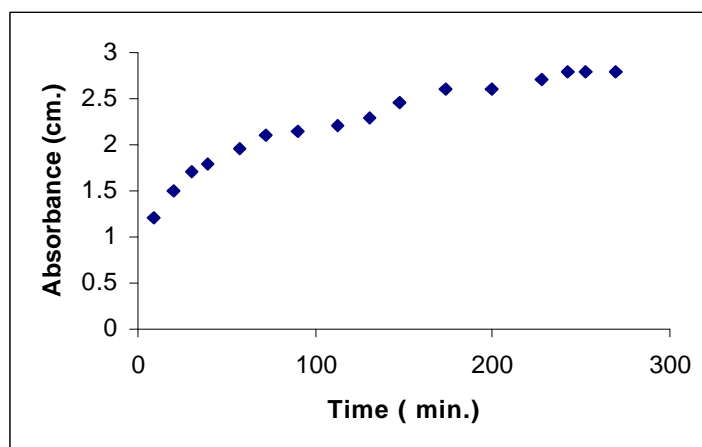


Figure 6. Absorbance (cm.) versus time at $\lambda = 462$ nm.
 $m = 2.1397$ g., $F = 15.56$ g. / min.

PERSPECTIVE AND CONCLUSION

We have measured the solubility of Red SM1P by three methods and obtained results with the same order of magnitude. We have introduced on-line UV-vis. Absorption spectrophotometry on dynamic extraction and are in accordance with the model proposed in the literature [4]. Those results will be applied to other dyes and in order to develop industrial dyeing.

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