CORRELATION OF DYES SOLUBILITIES IN SUPERCRITICAL CARBON DIOXIDE USING AN EXPANDED LIQUID MODEL

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ABSTRACT

The knowledge of dyes' solubilities in supercritical carbon dioxide is of great interest for the set up of the new process that substitutes water with the supercritical fluid as dyeing medium. In this work solubility measures of disperse orange 3, disperse blue 79, quinizarin and solvent brown 1, presented elsewhere [1,2], are correlated with an expanded liquid model. The model results from Hildebrand theory of dilute solutions [3] coupled with Flory-Huggins theory for systems in which the difference between molecular size of the components is large [4]. In this approach, activity coefficients of the dyestuffs at the working pressure and temperature have to be evaluated. The binary interaction parameter between the supercritical fluid and the dyestuff is found to be strongly dependent on solvent density and slightly dependent on temperature. According to literature, a polynomial dependence on density and temperature is assumed for the interaction parameter: starting from a literature regression function with nine adjustable parameters [5], a regression function with four and one with two fitting parameters have been tested. Absolute average percent deviations (AA%D) are compared with those of five well-known empirical equations with a comparable number of fitting parameters [2]. The expanded liquid model does not give reduction in deviations with respect to the tested empirical equations. Moreover, it requires a greater effort for the experimental evaluation and the estimation of some solute properties. These considerations make the solution model less attractive than the empirical equations in order to correlate dye solubility in supercritical carbon dioxide.

INTRODUCTION

Dry dyeing process with supercritical carbon dioxide is a good alternative to traditional dyeing. The use of the supercritical fluid as dyeing medium overcomes the problem of waste water treatment in the dyeing process [6]. In fact, since the dyestuffs are not soluble in the gas phase, they can be easily separated when the fluid is expanded from liquid-like to gas density. Besides, the drying process associated with traditional dyeing is avoided, thus resulting in a remarkable energy saving.

Phase behaviour and dye solubilities should be widely known for the design of this high-pressure process. Solubility is the maximum dye concentration in the fluid at given state conditions. This information, coupled with the partition coefficient between the solution and the fiber, can be used for defining the approximate operative conditions of the process. Therefore, prediction of solubility behaviour in a wide range of pressure and temperature should be the more accurate as possible. Unfortunately, most of the approaches for modelling the phase equilibrium of the supercritical fluid mixture are not predictive; at least one parameter should be obtained from regression of experimental data. In order to reduce the number of experimental measures that must be collected, the number of parameters of the model should be as small as possible.

In this work solubilities of disperse orange 3, disperse blue 79, quinizarin [1] and solvent brown 1 [2] are correlated with an expanded liquid model. The aim of the work is to reduce the number of parameters of a literature model with nine adjusted parameters [5], having, on the other hand, a fair correlation of experimental data. In effect, a model with many fitting parameters has the disadvantage to be applicable only when a substantial number of experimental measures is available. Besides, a comparison between the expanded liquid model and some empirical equations is carried out in order to find if the application of the solution model could be more advantageous for correlation of dye solubility.

I- THEORETICAL

Since density of a supercritical fluid is much similar to that of a liquid than a gas, Giddings et al. [7] proposed to treat the supercritical phase as an expanded liquid. With this approach, the solubility of a solute in a supercritical fluid is related to its activity coefficient in a manner similar to the solubility of a solute in a liquid solvent [8].

According to the dilute solution theory, when solubility of a solute (y_2) in a supercritical fluid is sufficiently low, y_2 can be expressed by the following equation:

$$y_2 = \frac{f_2^s}{f_2^0 \gamma_2^\infty} \qquad (1)$$

in which γ_2^∞ is the activity coefficient of the solute at infinite dilution, f_2^s is the fugacity of the pure solid at the same pressure and temperature of the system and f_2^0 is the fugacity of the solute in a reference state. It is convenient to choose as reference state the subcooled liquid at the temperature of the system and at the sublimation pressure of the solute. In this case, the ratio of fugacities is expressed by:

$$\ln\frac{f_2^s}{f_2^0} = \frac{\Delta H_{T_t}^{fus}}{R}\left(\frac{1}{T}-\frac{1}{T_t}\right)+\frac{1}{RT}\int_{Tt}^{T}\Delta c_p dT-\frac{1}{R}\int_{Tt}^{T}\frac{\Delta c_p}{T}dT+\int_{p_2^{sat}}^{p}\frac{\Delta v_2}{RT}dP \qquad (2)$$

If molar heat capacity variation between solid solute and liquid phase versus temperature can be considered negligible as well as solid molar volume variation versus pressure, the last three terms on the right end side of the equation can be neglected. Besides, assuming that triple point temperature for a heavy compound is almost equal to melting temperature and that fusion enthalpy is approximately constant, the previous equation can be rearranged as follows:

$$\ln\frac{f_2^s}{f_2^0} \cong \frac{\Delta H_2^{fus}}{R}\left(\frac{1}{T}-\frac{1}{T_2^m}\right) \qquad (3)$$

Then, the fugacity ratio is exclusively dependent on solute fusion properties, which can be easily evaluated experimentally.

Solid solute generally has a high molecular weight. Flory and Huggins have proposed that the activity coefficient at infinite dilution for mixture in which the components strongly differ from each other in molecular size can be expressed by the following equation:

$$\ln\gamma_2^\infty = \frac{v_2}{RT}\left[(\delta_1-\delta_2)^2-\beta_{12}\right]+1-\frac{v_2}{v_1}-\ln\frac{v_2}{v_1} \qquad (4)$$

where v_1 and v_2 are respectively solvent (1) and solute (2) molar volume, δ_1 and δ_2 are their solubility parameters and β_{12} is the binary interaction parameter connected with the intermolecular interactions between the solvent and the solute molecules.

Roughly, the interaction parameter depends on the chemical nature of the components and on the distance between the molecules in the system, that is related to system density. The interaction parameter is always obtained by regression from experimental data [9,10].

Solubility parameter of the supercritical carbon dioxide is expressed by the equation proposed by Giddings:

$$\delta_1 = 1.25 P_c^{1/2} \frac{\rho_1}{\rho_{liq}} \tag{5}$$

where ρ_{liq} is the density of the liquid phase at the boiling point. Solubility parameter of the solvent varies in proportion to gas density. This suggests that density, rather than the other state variables, i.e. pressure or temperature, is the crucial parameter for solubility determination [11]. Giddings considers the solvent power of the supercritical fluid as a function of the proximity to the critical point (*state effect*) and of its chemical nature (*chemical effect*). The state effect is related to ρ_r/ρ_{rl} while chemical effect to critical pressure.

Solubility parameter of the solute is usually evaluated by its definition:

$$\delta_2 = \left(\frac{\Delta U_2}{v_2} \right) \tag{6}$$

with the vaporization internal energy (ΔU_2) and the molar volume of the solid generally obtained by Fedors' group contribution method [12]. This method provides contributions both for internal energy and molar volume at 298.15 K. Effect of temperature on internal energy change of vaporization can be calculated by the following equation [12]:

$$\Delta U_{2,T} = \Delta U_2 \cdot \left\{1 + 1.13\alpha_2 (298 - T)\right\}^2 \cdot \left\{1 - \alpha_2 (298 - T)\right\} \tag{7}$$

where α_2 is the isobaric thermal expansion coefficient. The effect of temperature on solid molar volume is evaluated by an analogous expression. In most cases α_2 value is not available and in literature is assumed $1.0 \cdot 10^{-3}$ K^{-1} for all solid components for simplification [13].

II- MATERIALS AND METHOD

The experimental apparatus used to measure dye solubilities involved in the present work was described elsewhere [1]. It is a flow apparatus equipped with a bypass line that dilutes the saturated solution and allows high solubility measures without risk of clogging of the capillary valve when precipitation of the dye takes place. Solubilities of disperse orange 3, disperse blue 79, quinizarin and solvent brown 1 were measured at 353, 373 and 393 K at pressure between 160 and 300 bar. Quinizarin is not exactly a dyestuff for fabric dyeing but its chemical structure is similar to that of several anthraquinone dyes.

III- RESULTS AND DISCUSSION

Fusion properties of the compounds were experimentally measured by a differential scanning calorimeter (DSC) and are published elsewhere [2]. Thus, the ratio of fugacities is evaluated from Eq.3.

Solubility parameter of supercritical carbon dioxide is obtained from Eq.5. The fluid density at experimental conditions is measured via a massflow-meter [1].

Eq.6 is used for estimation of solubility parameters of the dyes. In Table 1 solid molar volume and vaporization energy are listed. Fedors' group contribution method is adopted.

In this work temperature effect on dye solubility parameter and solid molar volume is neglected because it does not affect results in terms of improvement in deviations between experimental and predicted data.

Compound	$\mathbf{v_2 \cdot 10^6}$ (m^3/mol)	**ΔU_2** (j/mol)
Disperse blue 79	477.0	230660
Disperse orange 3	196.4	121220
Quinizarin	128.8	174260
Solvent brown 1	199.6	125130

Table 1 Dyestuffs' molar volume and internal energy change at 298 K.

In the literature [5,9,10] the interaction parameter as a function of density is correlated with the polynomial:

$$\beta_{12} = a_0 + a_1 \cdot \rho + a_2 \cdot \rho^2 \qquad (9)$$

Besides, the parameters of the polynomial are considered temperature dependent and are correlated with an analogous quadratic law:

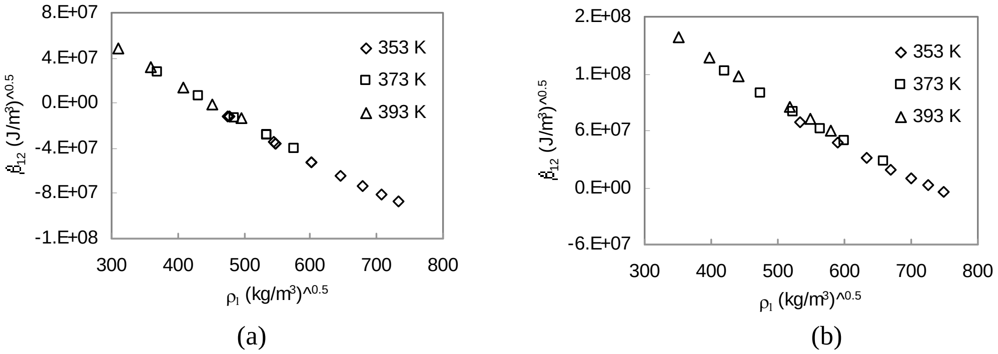
$$a_i = c_{0i} + c_{1i} \cdot T + c_{2i} \cdot T^2 \qquad (10)$$

This results in a number of fitting parameters equal to nine. In the first stage the same approach is used in this work. Parameters of the two quadratic polynomials were evaluated by minimization of the objective function:

$$F_{obj} = \sum \left(\frac{y_{2,sper} - y_{2,pred}}{y_{2,sper}} \right)^2 \qquad (11)$$

In the third column of Table 2 average absolute percent deviations (AA%D) between experimental and predicted data are presented. Solubilities of quinizarin at 393.2 K show the highest deviation. This phenomenon can be ascribed to two reasons: polymorphism of the solid phase [2] and high solubilities of quinizarin. In fact, quinizarin crystallizes in two different forms, which have different fusion properties. High solubilities can be another reason for model failure since dilute solution theory neglects the effect of concentration on the activity coefficient. The system quinizarin-CO_2 at high temperature cannot be treated as a *dilute solution*. The fact that the highest deviation is found at the highest pressures strengthens this hypothesis: in this condition solubility of quinizarin is about one order of magnitude larger than that of the other compounds.

In order to reduce the number of adjustable parameters of the regression function, trends of β_{12} versus solvent density are analyzed. In Figure 1 interaction parameter versus density for the system CO_2-Disperse orange 3 and CO_2-Disperse Blue 79 are shown as examples.



(a) (b)

Figure 1 Trend of β_{12} versus solvent density for Disperse orange 3 (a) and Disperse blue 79 (b).

The interaction parameter is strongly affected by system density. In fact the higher the density the stronger are the interactions between neighbouring molecules. As it is shown in the figure, the interaction parameter is found to be linear versus density and it seems almost independent of temperature. Therefore, a_2 in Eq.9 and c_{1i} and c_{2i} in Eq.10 are set equal to zero. In this case, the model just requires estimation of the two adjustable parameters that express the linear dependence on density while effect of temperature is neglected. As shown in the fifth column of Table 2, in some case deviations exceed acceptable values with this simplification. Finally, if a_2 in Eq.9 and c_{1i} in Eq.10 are set equal to zero, a linear dependence on both temperature and density can be assumed. In this approach the total number of fitting parameters is four. The four parameters version reaches a compromise between the fair accuracy in data correlation and the need of the minimum number of experimental measures to be collected for applying this model. It can be noticed in the last two columns of the table that the higher deviations are generally found at the lower temperature with the exception of quinizarin, for which the reason of the high deviations at high temperature has already been explained. At constant pressure, the lower the temperature the higher the density. As a consequence the quadratic dependence of β_{12} on density is less negligible as the density increases. Besides, since the binary interaction parameter is related to the activity coefficient via a logarithmic law, little variation of β_{12} causes large variation of the activity coefficient.

Compound	**T (K)**	**Expanded liquid model**		
		AA%D (9 par.)	**AA%D (4 par.)**	**AA%D (2 par.)**
Disperse Blue 79	353.2	4.61	17.3	101
	373.2	9.66	24.3	27.4
	393.2	3.55	16.2	29.0
	Mean	**5.87**	**19.1**	**55.1**
Disperse orange 3	353.2	3.32	10.7	22.1
	373.2	3.09	7.02	4.40
	393.2	6.06	6.85	14.4
	Mean	**3.88**	**8.80**	**15.5**
Quinizarin	353.2	8.17	20.6	24.2
	373.2	8.59	27.0	44.4
	393.2	19.1	34.5	55.3
	Mean	**11.3**	**25.5**	**35.9**
Solvent brown 1	353.2	3.77	16.5	17.2
	373.2	1.95	6.38	7.67
	393.2	4.74	9.95	9.78
	Mean	**3.51**	**11.0**	**11.8**

Table 2 Deviations of the expanded liquid model with nine, four and two parameters.

In order to evaluate the ability of this model to correlate dye solubility, the deviations are compared with those of five empirical and semiempirical equations that have been presented elsewhere [2]. In Table 3 the mean deviations of the literature correlations are reported.

Compound	**Mean AA%D**					
	Bartle et al. [14] (3 par.)	Mendez et al. [15] (3 par.)	Chrastil [16]. (3 par.)	Del Valle et al. [17] (4 par.)	Jouyban et al. [18]. (6 par.)	Exp. liquid model (4 par.)
Disperse blue 79	10.9	17.5	12.8	12.9	6.5	19.1
Disperse orange 3	12.3	15.4	5.1	4.5	4.6	8.80
Quinizarin	47.7	53.0	26.3	26.7	15.4	25.5
Solvent brown 1	7.4	10.3	6.8	6.6	3.9	11.0

Table 3 Deviations of some empirical equations.

The analysis of deviations highlights that the expanded liquid model does not give any substantial improvement in the correlation of experimental data and it even works worse in many cases. Deviations of the three parameters' equation proposed by Chrastil are lower than the four parameters expanded liquid model with the exception of quinizarin. Deviations of Jouyban et al. equation, which has six fitting parameters, are similar to those of the nine parameters expanded liquid model.

Then, the number of measures that must be collected in order to have an accurate trend of solubility as a function of pressure and temperature is not lowered when applying the expanded liquid model. On the other hand, it requires a greater effort in comparison with the empirical equations: there is an additional experimental effort, due to the evaluation of solute fusion temperature and enthalpy, and a computation effort, due to the estimation of some solute properties with a group contribution method.

CONCLUSIONS

Solubilities of disperse orange 3, disperse blue 79, quinizarin and solvent brown 1 in supercritical carbon dioxide were correlated with an expanded liquid model. Activity coefficients at dilute solution condition were evaluated from Flory-Huggins theory. Starting from a literature regression function with nine fitting parameters, the parameters of the regression function were reduced to four. The expanded liquid model is compared with some empirical correlations. The deviations are generally higher than those of the empirical equations and, moreover, the complication of solute properties' evaluation is added. These considerations make the solution model not attractive for correlation of dye solubility in supercritical carbon dioxide.

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