A NOVEL SOLUBILITY MODEL IN A SUPERCRITICAL CO_2

by

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This paper gives a semi-empirical formula for calculation of solubility of dyestuff in a supercritical CO_2 by dimensionless analysis, the obtained scaling law reveals that the solubility depends mainly on pressure and density of the supercritical CO_2.

Key words: *solubility, dyestuff, supercritical CO_2, scaling law, Bernoulli equation*

Introduction

Supercritical CO_2 is a green solvent, and it is widely used in supercritical fiber dyeing process [1-4]. Senyay-Oncel and Yesil-Celiktas [5] studied activity enhancement of cellulose treated with supercritical CO_2, and found that enzymes as catalysts in biochemical applications can be greatly improved by using supercritical fluids as potential media. Russler *et al.* [6] studied different approaches towards hydrophobic modification of bacterial cellulose aerogels with the alkyl ketene dimer (AKD) reagent, and found that if AKD modification was performed in supercritical CO_2, an unexpectedly high degree of loading was observed. However, the dye solubility in the supercritical CO_2 keeps still an open problem, though there are many semi-empirical formulae for this purpose [7-11]. For example:

$$T\ln(y_2 p) = a_1 + a_2\rho + a_3 T \tag{1}$$

$$\ln(y_2) = A + \frac{B}{T} + C\rho \tag{2}$$

$$\ln(y_2) = A' + \frac{B'}{T} + \left(C' + \frac{D'}{T}\right)\ln\rho \tag{3}$$

where y_2 is the solubility of dyestuff in mole fraction, T – the temperature, p – the pressure, ρ – the density of supercritical CO_2 [12], and the parameters in previous equations are constants, which can be determined experimentally. Equation (1) is the Mendez-Santiago-Teja

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formula [7], eq. (2) is the Kumar-Johnston formula [8], and eq. (3) is the Sung-Shim formula [9]. Though semi-empirical ones were widely used in supercritical fiber dyeing process, but all parameters in previous formulae are not dimensionless ones. Dimensionless analysis [13-15] should be adopted in the derivation of the semi-empirical formulae.

Dimensionless analysis

Dimensionless analysis has been widely applied in engineering to derive an empirical formula [13]. The solubility of dyes in supercritical CO_2 is a function of pressure, density and velocity of the supercritical CO_2:

$$y_2 = y_2(p, \rho, u) \tag{4}$$

Temperature is also a main factor affecting the solubility indirectly, it affects the density directly, so temperature is not involved in eq. (4).

By dimensionless analysis method, we write:

$$y_2 \propto p^a \rho^b u^c \tag{5}$$

where a, b, and c are constants. Balancing the dimensions of previous equation, we have:

$$[ML^{-3}] = [ML^{-1}T^{-2}]^a [ML^{-3}]^b [LT^{-1}]^c \tag{6}$$

or

$$\begin{cases} 1 = a + b \\ -3 = -a - 3b + c \\ 0 = -2a - c \end{cases} \tag{7}$$

Solving eq. (7), we have $a = n$, $b = 1 - n$, $c = -2n$, where n is a free parameter. So the solubility scales as:

$$y_2 \propto p^n \rho^{1-n} u^{-2n} \tag{8}$$

Therefore, we obtain a scaling law for solubility of dyestuff in a supercritical CO_2, which is:

$$y_2 \propto \left(\frac{\Pi}{E}\right)^n \rho \tag{9}$$

where $\Pi = p/\rho$ and $E = 1/2u^2$. According to Bernoulli equation, we have:

$$\Pi + E = B \tag{10}$$

where B is a Bernoulli constant. Equation (9) becomes:

$$y_2 \propto \left(\frac{\Pi}{B - \Pi}\right)^n \rho \tag{11}$$

or

$$y_2 = \alpha + \beta\left(\frac{\Pi}{B-\Pi}\right)^n, \quad \rho = \alpha + \beta\left(\frac{P}{B\rho - P}\right)^n, \quad \rho = \alpha + \beta\left(\frac{P}{\dfrac{P_0\rho}{\rho_0} - P}\right)^n \rho \tag{12}$$

where α and β are constants, P_0 and ρ_0 – the pressure and density, respectively, when the velocity is zero.

Table 1 shows the parameters and the average absolute relative deviation (AARD) between the measured and predicted results. Figures 1 and 2 compare our theoretical prediction with experimental data from [10].

Table 1. Parameters of eq. (12) and AARD between the experimental and predicted results

System	Parameters				AARD/%
	$\alpha \cdot 10^4$	$\beta \cdot 10^5$	$n \cdot 10^3$	$P_0/10^7$ [MPa]	
1-amino-4-hydroxyanthraquinone	–0.10236	1.1545	–1.9769	0.6793	7.36
1-hydroxy-4-nitroanthraquinone	–7.052	0.6236	–423	0.9217	5.6

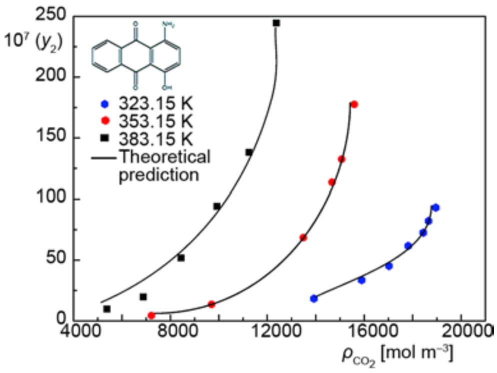

Figure 1. Comparison of solubilities of 1-amino-4-hydroxyanthraquinone in supercritical CO_2 with experimental data [10]

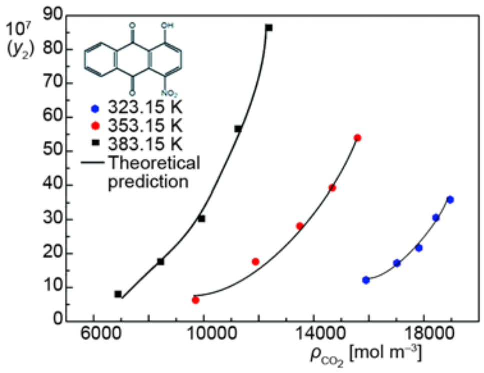

Figure 2. Comparison of solubilities of 1-hydroxy-4-nitroanthraquinone in supercritical CO_2 with experimental data[10]

Conclusion

We obtain a semi-empirical formula, eq. (12), for calculation of solubility of dyestuff in a supercritical CO_2 by dimensionless analysis. Using the state equation for supercritical CO_2 [10], temperature can be involved in eq. (12). Though the dimensionless analysis has been practiced many times in various fields, theoretical or experimental verification of eq. (12) is still much needed.

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