The solubility correlation of azobenzene derivatives in supercritical carbon dioxide: a short review

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Abstract. This short review highlights the solubility and correlation of four azobenzene derivatives, which have similar chemical structures, available in the literature. At the same phase equilibrium (at the temperature of 353.15 K), the solubilities of four azobenzene derivatives in supercritical carbon dioxide followed in the order of Disperse Red 82 > Disperse Red 13 > Disperse Blue 79:1 > Disperse Red 1. Five different kinds of density-based models were used to correlate the solubility data. Moreover, the solubilities of four azobenzene derivatives were also correlated thermodynamically by the model of the regular solution with the Flory–Huggins theory. It was found the Sung-Shim model (four parameters) has the lowest median AARD of 12.02 % of the solubility data over the entire conditions.

1. Introduction
Carbon dioxide has unique properties compared to other substances. It has unique properties of critical temperature (Tc = 304.15 K) and pressure (Pc = 7.383 MPa), respectively. Currently, in the textile industry, Supercritical carbon dioxide (scCO₂) dyeing process has been in attention. This technology has many advantages compared to conventional dyeing technology because carbon dioxide is nontoxic, non-flammable, recyclable, dyestuffs can be reused, and no additional chemical is required in the process. In addition, consumption energy can be saved because drying process is unnecessary so that dyeing time is short compared to the traditional dyeing technology. To the application and development of the Supercritical carbon dioxide (scCO₂) dyeing process requires specific knowledge of the phase equilibrium between dyestuffs and the supercritical carbon dioxide as a solvent, and a number of authors have discussed the dependence of solubility of dye in scCO₂ on both temperature and pressure, and have been presented in the literatures. Some investigators have found that the solubility of anthraquinones and azo derivatives are higher, static and dynamic methods have been used to measure the solubility of dyestuffs in supercritical carbon dioxide. We have measured and correlated the solubilities of anthraquinone derivatives in supercritical carbon containing the substituent groups —NO₂, —OH, —NH₂ [1-4] because some of the dyestuffs used in dyeing processes are configurated by these functional groups. In this short review, we highlight the solubility correlation and investigated the effects of functional groups of four azobenzene derivatives, which have similar chemical structures containing the substituent groups of —NO₂ available in the literature [5-6], namely, C.I. Disperse Red 1, C.I. Disperse Red 13, C.I. Disperse Red 82, and C.I. Disperse Blue 79:1. The solubility data obtained from the literature were correlated with the density based models, the Chrastil [7], the Sung–Shim [8], Bartle et al [9], Kumar-Johnston [10], and the Mendez-Santiago–Teja [11] models. Moreover, the solubilities of four azobenzene derivatives were also correlated thermodynamically by the model of regular solution with the Flory–Huggins theory [12].
2. Solubility of four azobenzene derivatives in supercritical carbon dioxide

In this study, we used the solubility data available in the literature measured by Shinoda et al.[5] and Lin et al.[6]. Table 1 presents the Physical properties of C.I. Disperse Red 1, C.I. Disperse Red 13, C.I. Disperse Red 82, and C.I. Disperse Blue 79:1.

Table 1. The physical properties of C.I. Disperse Red 1 and C.I. Disperse Red 13, C.I. Disperse Red 82, and C.I. Disperse Blue 79:1.

|          | Red 1    | Red 13   | Red 82   | Blue 79:1 |
|----------|----------|----------|----------|-----------|
| CAS number | 2872-52-8 | 3180-81-2 | 30124-94-8 | 3618-72-2 |
| Mw        | 314.34   | 348.78   | 439.43   | 625.39    |
| \(T_m\) / (K) | 431.15\(^a\) | 406.15\(^a\) | 402.3\(^b\) | 422.15\(^c\) |
| \(\Delta h_m\) / (kJ · mol\(^{-1}\))\(^d\) | 36.93    | 37.77    | 52.15    | 59.55     |
| \(v_2^s\) / (m\(^3\) · mol\(^{-1}\))\(^e\) | 2.23 · 10\(^{-4}\) | 2.53 · 10\(^{-4}\) | 3.04 · 10\(^{-4}\) | 3.86· 10\(^{-4}\) |
| \(T_c\) / (K)\(^e\) | 946.28   | 951.96   | 901.49   | 952.37    |
| \(P_c\) / (MPa)\(^e\) | 2.025    | 1.924    | 1.3899   | 1.252     |
| \(\omega\)\(^f\) | 1.231    | 1.251    | 1.171    | 0.931     |

\(^a\) Observed by Kozak et al.[13] \(^b\) Observed by Suesat et al. [14] \(^c\) Observed by Thiel et al.[15]
\(^d\) Estimated by Jain et al. method [16] \(^e\) Estimated by Fedors method [17] \(^f\) Estimated by Edmister method [18]

Figure 1. The solubility at temperature of 353.15 K of C.I. Disperse Red 82, C.I. Disperse Red 13, C.I. Disperse Blue 79:1, and C.I. Disperse Red 1 against density of CO\(_2\) \(\rho\) / (mol·m\(^{-3}\)).

The same equilibrium condition (the temperature of 353.15K) is shown in the figure 1. It was found the C.I. Disperse Red 82 is the most soluble in the supercritical carbon dioxide over the entire pressure
The magnitudes of the solubilities of four azobenzene derivatives in supercritical carbon dioxide are in the order of Disperse Red 82 > Disperse Red 13 > Disperse Blue 79:1 > Disperse Red 1. The results showed that the additional —CN group on the Disperse Red 82 cause the solubility was much better in carbon dioxide than other structures. It was found that presence of —CN group significantly decreased the polarity of dye molecule so the solubility of dye was higher because supercritical carbon dioxide is nonpolar. In addition, the solubility of azobenzene derivatives in supercritical carbon dioxide were independent of the molecular weight as shown in the table 1, the level of the molecular weight of four azobenzene derivatives were Disperse Blue 79:1 > Disperse Red 82 > Disperse Red 13 > Disperse Red 1.

3. Correlations

The solubility data obtained from literature were correlated using several types of semi-empirical equations, expressed in terms of pressure, temperature, and density of CO\(_2\), proposed previously by the Chrastil [7], the Sung–Shim [8], Bartle et al. [9], Kumar-Johnston [10], and the Mendez-Santiago–Teja [11]. These equations have three or more parameters to be adjusted to the solubility values. In the Bartle et al. model, \(P_{\text{ref}}\) was set 700 kg/m\(^3\) used as a reference density, \(P_{\text{ref}}\) is set 0.1 MPa as a standard pressure. Table 2 summarizes the density-based models and equations used. Figure 3 summarizes the average absolute relative deviation (AARD) for four azobenzene derivatives. It was found that Sung-Shim model has lower average absolute relative deviation (AARD) than that of other models as illustrated in the figures 2-3. However, the correlation of Mendez-Santiago–Teja obtained the higher average absolute relative deviation (AARD), about 40 \%. Table 3 shows the parameters of the azobenzene derivatives system used and average absolute relative deviation (AARD) between the solubility data and calculated values. Furthermore, by assuming that no considerable solubility of the sc-CO\(_2\) in the solid phase, the solubility of four azobenzene derivatives were correlated by the thermodynamic model of solid-liquid equilibria. A detailed explanation of the calculation procedure of the thermodynamic criteria has been reported elsewhere [1-4]. We briefly explain the calculation procedure in this study. We used the regular solution model combined with the Flory – Huggins equation [2],[12]:

\[
\ln y_2 = \frac{\Delta h^0}{RT} \left( \frac{T}{T_m} - 1 \right) - \frac{v_2}{RT} (\delta_1 - \delta_2)^2 - \ln \left( \frac{v_2}{v_1} \right) - 1 + \frac{v_2}{v_1} \tag{1}
\]

where \(T\) and \(\Delta h^0\) are the melting temperature and melting enthalpy of solid solute, respectively. The \(v_1\) and \(v_2\) are the molar volume of sc-CO\(_2\) and solid solute. The solubility parameters of sc-CO\(_2\) were calculated by the method of Giddings et al.[19]

\[
\delta_1/(\text{MPa})^{0.5} = 8.0325(P_c/\text{MPa})^{0.5} \left( \frac{\rho_r}{\rho_c} \right)^{2.66} \tag{2}
\]

The \(\rho_r\) ( = \(\rho / \rho_c\)) is the reduced CO\(_2\) density, \(\rho_c\) the critical density, and \(P_c\) is the critical pressure of CO\(_2\). The solute solubility parameter was assumed to be dependent on CO\(_2\) density, so can be expressed as:

\[
\delta_2 = a + b\rho_{\text{CO}_2} \tag{3}
\]

The average absolute relative deviation (AARD \%) for the systems of \(N_D\) data points in this study can be calculated by:

\[
\text{AARD(\%)} = \frac{100}{N_D} \sum_{n=1}^{N_D} \left| y_{2,n}^{\text{exp}} - y_{2,n}^{\text{cal}} \right| y_{2,n}^{\text{exp}} \tag{4}
\]
Table 2. Density-based models and equations used.

| Models                        | Equations                                           | Ref.  |
|-------------------------------|-----------------------------------------------------|-------|
| Mendez-Santiago – Teja        | $T \ln (y_2P) = A + B\rho + CT$                    | [11]  |
| Chrastil                      | $\ln y_2 = A + \frac{B}{T} + C \ln \rho$           | [7]   |
| Bartle et al.                 | $\ln \left(\frac{y_2P}{P_{ref}}\right) = A + B(\rho - \rho_{ref}) + \frac{C}{T}$ | [9]   |
| Kumar – Johnston              | $\ln y_2 = A + \frac{B}{T} + C \rho$               | [10]  |
| Sung – Shim                   | $\ln y_2 = A + \frac{B}{T} + \left(\frac{C + D}{T}\right)\ln \rho$ | [8]   |

Table 3. Parameters of the Azobenzene derivatives system used and average absolute relative deviation (AARD) between the solubility data and calculated values.

| System                              | Parameters | AARD (%) |
|-------------------------------------|------------|----------|
|                                    | $A$        | $B$      | $C$       | $D$       |          |
| **Chrastil**                        |            |          |           |           |          |
| C.I. Disperse Red 1 + CO$_2$        | -43.323    | -9437.5  | 6.0339    |           | 20.09    |
| C.I. Disperse Red 13 + CO$_2$       | -46.76     | -8203.7  | 6.1067    |           | 19.58    |
| C.I. Disperse Red 82 + CO$_2$       | -68.912    | -4359.3  | 7.3209    |           | 18.06    |
| C.I. Disperse Blue 79:1 + CO$_2$    | -65.355    | -5337.1  | 7.1501    |           | 13.38    |
| **Mendez-Santiago – Teja**          |            |          |           |           |          |
| C.I. Disperse Red 1 + CO$_2$        | -14443     | 0.24584  | 35.114    |           | 59.96    |
| C.I. Disperse Red 13 + CO$_2$       | -13281     | 0.24884  | 32.454    |           | 54.92    |
| C.I. Disperse Red 82 + CO$_2$       | -9488.4    | 0.28638  | 20.967    |           | 33.19    |
| C.I. Disperse Blue 79:1 + CO$_2$    | -10457     | 0.28262  | 23.024    |           | 22.52    |
| **Bartle et al.**                  |            |          |           |           |          |
| C.I. Disperse Red 1 + CO$_2$        | 26.167     | -11391   | 0.015806  |           | 41.94    |
| C.I. Disperse Red 13 + CO$_2$       | 23.501     | -10179   | 0.015994  |           | 38.89    |
| C.I. Disperse Red 82 + CO$_2$       | 12.409     | -6016.3  | 0.017429  |           | 29.02    |
| C.I. Disperse Blue 79:1 + CO$_2$    | 14.517     | -7063.3  | 0.017204  |           | 14.19    |
| **Kumar – Johnston**               |            |          |           |           |          |
| C.I. Disperse Red 1 + CO$_2$        | 7.1483     | -10008   | 0.00060037|           | 40.71    |
| C.I. Disperse Red 13 + CO$_2$       | 4.3513     | -8796.7  | 0.00060866|           | 39.19    |
| C.I. Disperse Red 82 + CO$_2$       | -7.4703    | -4740.8  | 0.00067208|           | 30.14    |
| C.I. Disperse Blue 79:1 + CO$_2$    | -5.2058    | -5787.8  | 0.0006622 |           | 13.39    |
| **Sung – Shim**                    |            |          |           |           |          |
| C.I. Disperse Red 1 + CO$_2$        | 21.718     | -32853   | -0.89301  | 2489.4    | 12.98    |
| C.I. Disperse Red 13 + CO$_2$       | 26.789     | -34682   | -1.7264   | 2815.1    | 8.86     |
| C.I. Disperse Red 82 + CO$_2$       | 19.446     | -37588   | -2.1001   | 3540.7    | 15.05    |
| C.I. Disperse Blue 79:1 + CO$_2$    | -10.905    | -25814   | 1.3445    | 2181.9    | 11.20    |
Figure 2. Plot of mole fraction $10^5 y_2$ against density of $\rho_{\text{CO}_2}/(\text{mol} \cdot \text{m}^{-3})$ to correlate results for C.I. Disperse Red 82 (a), C.I. Disperse Red 13 (b), C.I. Disperse Blue 79:1 (c), and C.I. Disperse Red 1 (d) from Sung-Shim model.

Figure 3. Summarizes the average absolute relative deviation ($AARD$) for four azobenzene derivative
4. Conclusions
The solubility correlation of four azobenzene derivatives which have similar chemical structures taken from available literature has been studied. At the same phase equilibrium (at the temperature of 353.15 K), the solubilities of four azobenzene derivatives in supercritical carbon dioxide followed the order of Disperse Red 82 > Disperse Red 13 > Disperse Blue 79:1 > Disperse Red 1. Five different kinds of density-based models were used to correlate the solubility data. Moreover, the solubilities of four azobenzene derivatives were also correlated thermodynamically by the model of the regular solution with the Flory–Huggins theory. It was found that the Sung-Shim model (four parameters) has the lowest median AARD of 12.02% of the solubility data over the entire conditions.

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