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# Solubility and data correlation of a reactive disperse dye in a quaternary system of supercritical carbon dioxide with mixed cosolvents

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ABSTRACT

Mixed cosolvents involving acetone and water were applied in hydrophobically supercritical carbon dioxide medium for modifying the solubility behavior of a new reactive disperse orange SCF-AOL2 dye. Then the equilibrium solubility of the dye solute in the quaternary system of supercritical carbon dioxide with the mixed cosolvents was measured at temperature from 333.2 K to 393.2 K and pressure from 8.0 MPa to 22.0 MPa with an equilibrium time of 60 min in a home-built batch circulation system. The experimental results show that a significant improvement of the dye solubility and its behavior was achieved in the presence of the mixed cosolvents in supercritical carbon dioxide, especially with the tested system pressure in different solubility isotherm curves. Moreover, the achieved experimental data were further correlated, validated and predicted successfully by employing several typically semi-empirical models for the quaternary system with mixed cosolvents. It is most important that a new and specially derived model based on the conventional and modified Mendez-Santiago–Teja ones was also proposed and successfully applied to the quaternary system with a significant improvement and highest accuracy than the employed other ones. Furthermore, better correlations were also achieved from the conventional Chrastil and the Del Valle-Aguilera models than other ones for the employed system.

## 1. Introduction

Textile dyeing with water free, especially with supercritical carbon dioxide (SCF-$CO_2$) medium, has received more and more attractions in its cleaner production property and economical interest due to some rapid developments and dramatic breakthroughs of this technology in machinery, special dyes and various applicable processes etc., in recent years [1–9]. With regard to a commercial application purpose of this technology, the solubility behavior of different dye solutes in the hydrophobic medium of supercritical carbon dioxide fluid plays a fundamental and important role in the dye selection, color matching, process design and control, and the improvement of process efficiency for achieving some desired shades from customers, etc. [3,10–13]. During the last decades, numerous researches have been carried out to investigate the solubilities or phase behaviors of different dye solutes, even as well as various other organic compounds [14–17] in supercritical carbon dioxide medium for facilitating the application of this technology in practice [2,5,12,18–25]. Particularly, most of those researches are mainly concentrated on disperse organic dyes. However, despite of the considerable advantages of supercritical carbon dioxide fluid acted as a medium for the textile manufacturing in the viewpoint of cleaner production with water free [4,26–27], it is a really hydrophobic medium due to the linearly symmetrical structure of carbon dioxide molecule, and is also hardly to form some specially and powerfully intermolecular interactions such as hydrogen bonds with either solutes or other solvents. Consequently, supercritical carbon dioxide is also limited to be a manufacturing medium during its practical applications in some fields, such as in textile industry for some coloration processes by employing some of the dyestuffs with high polar and complicated molecular structures, due to their poor solubility and coloration in this medium.

Therefore, in recent years, there are many strategies adopted by different researchers from the world in order to improve the solubility behaviors of dye solutes in the hydrophobic medium. Among all those strategies, One of the most important and powerful strategies is to add a small amount of cosolvent into the supercritical fluid medium, which has been proved to be an efficient and readily method to significantly enhance the solubility of some polar and/or complicated structural dye solutes [28–32]. Therefore, improved process efficiencies and shades for substrate colorations could be readily achieved in supercritical carbon dioxide

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**Notation table**

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|---|---|
| $a$, $b$ | the parameters of the Chrastil model in Eq. (6); |
| $A$ | the characteristic absorbance of the standard addition dye solute at its maximum wavenumber of 450.0 nm ($\lambda_{\max}$) in ethanol; |
| $A_0$, $A_1$, $A_2$, $A_3$ | the model parameters of typical Del Valle-Aguilera model in Eq. (8); |
| AARD (%) | the average absolute relative deviation; |
| $A_i$ | the characteristic absorbance of an individually sampled dye solute at its maximum wavenumber of 450.0 nm ($\lambda_{\max}$) in ethanol; |
| $B_0$, $B_1$, $B_2$ | the parameters of the typical Mendez-Santiago–Teja model in Eq. (9); |
| $C^*$ | individual concentration of the standard addition dye solute in ethanol with a unit of g $L^{-1}$; |
| $C_i$ | the solubility of the SCF-AOL2 dye solute in pure supercritical carbon dioxide medium without the cosolvents in a unit of g $L^{-1}$ at a corresponding system condition of the $C_i^{Cos}$; |
| $C_i^{Cos}$ | the solubility of the reactive disperse orange SCF-AOL2 dye in supercritical carbon dioxide fluid with the presence of the mixed cosolvents in a unit of g $L^{-1}$; |
| $C_i^{cos\ exp}$, $C_i^{Cos\ cal}$ | the experimental and calculated solubilities in the employed quaternary system with the mixed cosolvents, respectively; |
| $D_0$, $D_1$, $D_2$ | the parameters of the typical Bartle model in Eq. (10); |
| $E$ | The cosolvent enhancement effect; |
| $i$ | 1, 2, 3…$n$, refers to the individual experiments performed under different system conditions; |
| $J_0$, $J_1$, $J_2$, $K_0$, $K_1$, $K_2$, $K_3$, $Z_0$, $Z_1$, $Z_2$, $Z_3$, $Z_4$ | the adjustable parameters of the typical and modified Mendez-Santiago–Teja models in Eq. (11)–(13); |
| $k$ | the association number of the supercritical medium to one molecule of the dye solute; |
| $MCO_2$, $M_{Dye}$ | the molecular weight of carbon dioxide and the reactive disperse orange SCF-AOL2 dye; |
| $ML_{i3}$, $ML_{i4}$ | the utilized molar quantities of the cosolvent components of acetone and water at an individual system condition, respectively. |
| $OBF$ | the objective function; |
| $P$ | the system pressure (MPa); |
| $P_2^{Sub}$ | the sublimation pressure of solute; |
| $P_c$ | the reference pressure assumed as o.1 MPa [38]; |
| $P^{Std}$ | the standard pressure and equal to 0.1 MPa [35]; |
| $R$ | refers to a solvent; |
| $S$ | refers to a solute; |
| $T$ | the absolute temperature (K); |
| $V$ | the volume of the sampling tube, which is 0.01 L in this work; |
| $v$ | the volume of the collected reactive disperse orange SCF-AOL2 dye solution from an individual experiment, which is 0.1 L in this work; |
| $X_3$ | the mole fraction of a cosolvent; |
| $Y_3$, $Y_4$ | the mole fractions of the cosolvent components of acetone and water in this work, respectively, and $Y_3Y_4 \neq 0$; |
| $y_i^{\ Cos}$ | the solubility of the reactive disperse orange SCF-AOL2 dye in supercritical carbon dioxide fluid with the presence of the mixed cosolvents in a mole fraction at an individual system condition; |
| $\rho_c$ | the reference density of pure supercritical carbon dioxide fluid assumed as 15.91 mol $L^{-1}$ or 700 kg $m^{-3}$ [38]; |
| $\rho_i$ | the density of pure supercritical carbon dioxide in a unit of Kg $m^{-3}$ or mol $L^{-1}$ at a corresponding condition of $C_i^{Cos}$ or $y_i^{\ Cos}$, which was calculated by an online program [40] based on the Stryjek and Vera modification of the Peng–Robinson equation of state (PRSV) [41]; |

fluid with the presence of a very small amount of cosolvents. Generally, the frequently employed cosolvents are some polar organic and/or inorganic compounds with relative small chemical structures and readily volatile properties. Especially, they could act as a hydrogen bond donor and/or an acceptor for dye solutes as well as others cosolvents in the system, in order to reinforce solvation effect by forming some association complexes, such as the conventional cosolvents of acetone, ethanol, methanol and dimethylsulphoxide, etc. [30,33]. Up to date, there are some experiments reported about the dye solubilities in supercritical carbon dioxide fluid with the presence of different cosolvents [28–32]. Lee et al. [31] reported the solubility of Disperse Red 82 and modified Disperse Yellow 119 in supercritical carbon dioxide with ethanol as a cosolvent, and found that the solubility increases substantially up to (9 to 25)-fold, by adding 5 mol% of ethanol to the supercritical fluids. Tsai et al. [30] measured the solubility of Disperse Yellow 54 in supercritical carbon dioxide with or without cosolvent, and the results showed that the magnitudes of equilibrium solubility could be effectively enhanced in the presence of cosolvents of ethanol or dimethyl sulfoxide. Bae et al. [29] investigated the influence of cosolvent on dye solubility in supercritical carbon dioxide, and their experiments showed that the solubility of non-volatile solid such as disperse dye in supercritical fluid was significantly increased by adding a small amount of co-solvent into the fluid. Banchero et al. [28] also investigated the solubility of three disperse dyes in a mixture of $CO_2$ and ethanol, and revealed that the addition of ethanol caused a huge solubility increase that was roughly related to the molecular weight of the dyestuff. Moreover, these obtained experimental results above with the presence of cosolvents were also correlated, validated and predicted by different models, such as the conventional density based semi- and empirical models for binary system as like the Chrastil, the Mendez-Santiago Teja, the Bartle, the Del valle- Aguilera models, etc., and even with the Peng–Robinson equation of state (EOS), or an expanded liquid model, etc. [28–31]. It is most important that some modified and expanded versions of the Chrastil and the Mendez–Santiago Teja equations for ternary system with cosolvents are also developed for correlation and prediction of the solubility data of dye and other solid solutes in mixed media [28,34,35]. Obviously, all these research work and innovation attempts above contribute to an important,

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