

# ANALYSIS OF THE CO-SOLVENT EFFECT ON DYE SOLUBILITY

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A thermodynamic model was developed using the chemical theory to describe enhancement of dye solubility in supercritical carbon dioxide due to cosolvent effect as a function of density of the fluid phase. This solvation-association model was formulated based on the physical and chemical interactions between cosolvent molecules and cosolvent and solute molecules. The solubility of C. I. Disperse Blue 60 (B60) in supercritical CO<sub>2</sub> loaded with either acetone or ethanol as a cosolvent was measured at pressures between 10 and 30 MPa and at temperatures between 313.15 and 423.15 K. The solubility varied as a quadratic function of cosolvent concentration. For nonpolar B60, the solubility could be described with only the physical interaction. For polar C. I. Disperse Red 60 (R60), the chemical interaction as well as physical interaction was also necessary to explain the solubility enhancement by cosolvent. The chemical interaction was attributed to the formation of hydrogen bonds and charge transfer complexes between the solute and the cosolvent molecules and was estimated by correlating the enhanced solubility with density.

## INTRODUCTION

The conventional wet-dyeing industry that discharges a lot of wastewater containing highly concentrated, very little biodegradable surfactants has been continuously raising pollution problems worldwide. Among the several researches aiming to replace the conventional process, supercritical fluid dyeing (SFD) process has been particularly drawing attention as it is an environmentally friendly process that does not require any surfactant nor dispersing agent[1,2]. Furthermore, energy consumption may be only half that of the conventional dyeing process as the drying step is not necessary in the SFD process.

To develop and design this new process, a lot of basic dye solubility data are necessary. These dye solubilities in supercritical fluids (SCFs) have been measured[3-7]. Although there have been a lot of research on solid solubility in SCF, the fluid-phase behavior of solids with very high molecular weights has not been fully understood yet. To our knowledge, thermodynamic analysis of solubility of the disperse dyes with molecular weights over 300 g/g mol has not been reported yet as their critical properties and vapor pressures are not known. Only empirical equations have been used to correlate the solubility of large solids with pressure or density of the fluid.

The solubility of solid materials in SCFs dramatically increased when a small amount of cosolvent was added to the fluid[8-11]. Dobbs et al.[8] measured the solubility enhancement by adding nonpolar or polar cosolvent and correlated the solubility with a modified van der Waals equation of state and predicted it qualitatively by calculating the attraction constants. Ekart et al.[10] used the SCF chromatographic technique to build a database of cosolvent effects for a variety of cosolvents and solutes,

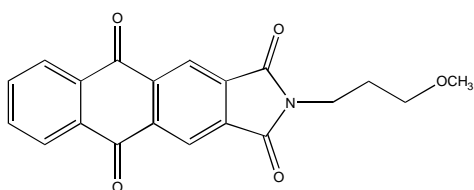
which may be resulted from the specific interactions due to the formation of hydrogen bonds, charge transfer complexes and dipole-dipole couplings between the solute and cosolvent molecules. Muthkumaran et al. [6] measured the solubility of R60 enhanced in supercritical CO<sub>2</sub> by adding a polar cosolvent such as acetone and ethanol and they correlated the solubility data fairly well using dilute-solution theory with lattice-fluid-hydrogen-bonding model. Anderko[11] proposed the AEOS (association + equation of state) model for associating polar substances that form hydrogen bonds. Alsten et al.[9] suggested a combined chemical-physical model for the acridine-methanol-CO<sub>2</sub> system. Their model described the cosolvent effect on the solid solubility fairly well.

In this work the solubility enhancement was measured by adding a small amount of ethanol or acetone into supercritical CO<sub>2</sub>. To describe the cosolvent effect on dye solubility, we developed equations using the chemical theory covering the physical and chemical interactions between solute-cosolvent and cosolvent-cosolvent molecules. The experimental solubility data of disperse dyes in pure supercritical CO<sub>2</sub> was correlated with Peng-Robinson equation of state (EOS).

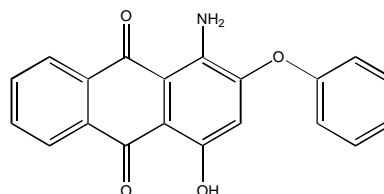
## EXPERIMENTAL SECTION

### Materials

C. I. Disperse Blue 60 (Figure 1) was obtained from LG Chemical. CO<sub>2</sub> with purity of 99% was obtained from Daedong Oxygen. Ethanol of 99.5% and special grade acetone were obtained from Kanto Chemical and Yakuri Pure Chemical, respectively.



C. I. Disperse Blue 60



C. I. Disperse Red 60

**Figure 1** : Molecular structures of nonpolar and polar disperse dyes used in this study.

### Experimental Equipment

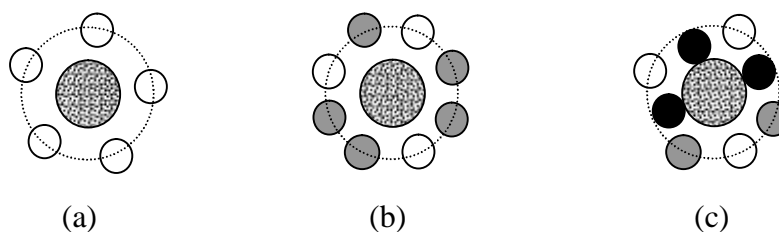
A closed-loop (batch) solid-fluid equilibrium apparatus was installed in a constant-temperature air bath that was controlled within  $\pm 1$  K. A high-pressure magnetic pump was used to circulate the dye mixture along the loop. A pressure transducer (Sensotec, Model TJE) and signal indicator (Sensotec, Model GM) were used to read the pressure to  $\pm 0.01$ MPa.

### Experimental Procedures

A known amount of cosolvent, either acetone or ethanol, was injected into the equilibrium cell at a constant temperature. Then, liquid CO<sub>2</sub> was pumped with a high-pressure metering pump (LDC/Milton Roy) into the system to make a desired pressure. Now the mixture in the isolated equilibrium system was circulated with the magnetic pump for 120 minutes until the equilibrium solubility of the dye was attained. Then, the dissolved dye was collected with ethanol. The dye-ethanol solution was analyzed by UV/Visible spectrometer (Perkin-Elmer Lambda 40). Ethanol remaining in the cell was completely removed by flushing with air. The experimental uncertainty is within  $\pm 5\%$ .

### THEORETICAL CONSIDERATION

In nonpolar SCF, the dye molecules sublime into the fluid phase and are surrounded by the fluid molecules as shown in Figure 2(a). In the presence of co-solvent, however, the sublimated dye molecules are surrounded by both the fluid and co-solvent molecules with only physical forces (Figure 2(b)). And then, some of the co-solvent molecules approach closer to the dye molecule at the center forming hydrogen bonds or charge transfer complexes, lowering the energy state of the dye molecule (Figure 2(c)). Highly polar cosolvent may form associated dimers, trimers, and so on.



**Figure 2** : Schematic diagram for solvation of dye molecules (large dotted circle) in (a) pure nonpolar fluid ( $\circ$ ), (b) mixture of fluid and cosolvent with physical molecular attractions ( $\odot$ ), and (c) mixture of fluid and cosolvent with both physical ( $\odot$ ) and chemical ( $\bullet$ ) attractions.

If the cosolvent is a polar compound, thermodynamic properties may be determined by the chemical interaction between polar species and the physical interaction between all the species in the solution[11]. Lambert[12] divided the second virial coefficient into physical and chemical parts. Smirnova [13] separated the compressibility factor on the basis of statistical thermodynamics as

$$Z = Z^{phys} + Z^{chem} - 1 \quad (1)$$

where  $Z^{phys}$  and  $Z^{chem}$  are the physical- and chemical contributions, respectively, to the compressibility factor.  $Z^{phys}$  can be determined by an equation of state such as Peng-Robinson EOS.  $Z^{chem}$  represents the extent of reduction in the overall number of moles due to the chemical forces leading to association[11].

Kumar and Johnston defined a new fugacity coefficient of  $i$ ,  $y_i = f_i Z$ , based on the density of the fluid[14]. Some theoretical treatments yield the following relationship for a solid solute:

$$\ln y_A = \ln y_A^{phys} + \ln y_A^{chem} \quad (2)$$

The fugacity of A in the fluid phase may be written as  $f_A = rRT y_A y_A$ . As the chemical potential of the apparent solute,  $m_{A_0}$ , is the same as that of the true monomer,  $m_A$ , for both the actual- and the standard states, we get  $y_{A_0} y_{A_0} = y_A y_A$ . Some molecules of solute A initially placed in the system may be chemically solvated with co-solvent C,

while some other molecules of A still exist as monomers that have only physical interactions. Because the physical interactions occur among the monomers of A that are not involved in the chemical solvation,  $\mathbf{y}_{A_0}^{phys} = \mathbf{y}_A^{phys}$ . Therefore,  $\mathbf{y}_{A_0}^{chem} = y_A / y_{A_0}$ .

We developed equations for a number of solvation reactions of solute A and cosolvent C in a similar manner to Anderko's[11], assuming that solute does not associate but solvates with up to k molecules of cosolvent. By multiplying all the equilibrium constants for the above solvation, assuming that the equilibrium constant,  $K_{AC_i}$ , is independent of the number of solvation, we get

$$K_{AC}^k = \frac{\mathbf{z}_{AC_k} \tilde{\mathbf{r}}}{(\mathbf{z}_A \tilde{\mathbf{r}})(\mathbf{z}_C \tilde{\mathbf{r}})^k} \quad (3)$$

where  $\zeta$  is the true mole fraction and  $\tilde{\mathbf{r}}$  is the true molar density. Further treatment yields that

$$y_{A_0} = y_A \left[ 1 + \sum_{i=1}^k (K_{AC} y_C \mathbf{r})^i \right] \quad (4)$$

The parenthesis in eq 4 includes only the chemical contribution, i.e.,  $1/\mathbf{y}_{A_0}^{chem}$ , "cosolvent effect" that enhances the solubility of solute through association and chemical solvation.

The value of  $y_{A_0}$  is evaluated using the mole fraction of cosolvent monomer,  $y_C$ , assuming that up to  $q$  cosolvent molecules associate to form complexes. Assuming equal consecutive association enthalpies, we can get equations for the equilibrium association constant,  $K_{CC}$ , and for the number of moles of monomer C. If only cosolvent dimers are formed, the degree of association is 2 and we have the ratio of the true and apparent moles as follows:

$$y_C = \frac{-1 + \sqrt{1 + 8K_{CC} y_{C_0} \mathbf{r}}}{4K_{CC} \mathbf{r}} \quad (5)$$

$$\frac{n_T}{n_0} = \frac{8K_{CC} \mathbf{r} - 4K_{CC} y_{C_0} \mathbf{r} - 1 + \sqrt{1 + 8K_{CC} y_{C_0} \mathbf{r}}}{8K_{CC} \mathbf{r}} \quad (6)$$

If infinite number of cosolvent molecules associate, we have

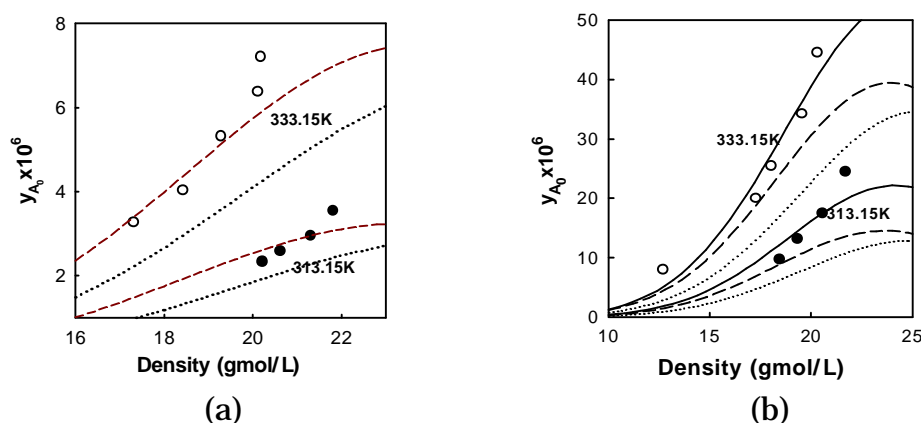
$$y_C = \frac{(1 + 2K_{CC} y_{C_0} \mathbf{r}) - \sqrt{1 + 4K_{CC} y_{C_0} \mathbf{r}}}{2y_{C_0} (K_{CC} \mathbf{r})^2} \quad (7)$$

$$\frac{n_T}{n_0} = \frac{2K_{CC} \mathbf{r} (1 - y_{C_0}) - 1 + \sqrt{1 + 4K_{CC} y_{C_0} \mathbf{r}}}{2K_{CC} \mathbf{r}} \quad (8)$$

## RESULTS AND DISCUSSION

### *Nonpolar dye with polar cosolvents*

The solubility of B60 enhanced with polar cosolvent in supercritical CO<sub>2</sub> is shown in Figure 3(a). The solubility increased up to 80% by adding 4.3mol% ethanol and acetone at 313.15 and 333.15 K. B60 molecules cannot associate since they do not have any polar groups. It has nonpolar methyl- and benzyl groups and slightly polar carbonyl and ether groups, making only the physical solvation. The dotted lines were obtained by correlation of the experimental sorption data with Peng-Robinson EOS. The dashed lines were obtained considering the physical contribution in addition to the solubility in pure CO<sub>2</sub>. The pressure-based fugacity coefficient  $f_A$  was obtained from the density-based fugacity coefficient,  $y_A$ . The calculated solubility isotherms fit the experimental data fairly well for both cosolvents, acetone and ethanol. From the above results we can conclude that there was no chemical but physical contribution to the solubility for nonpolar B60 molecules.



**Figure 3** : Solubility of (a) B60 and (b) R60 in supercritical CO<sub>2</sub> at 313.15 and 333.15 K enhanced with 4.3 mol% ethanol. — Solubility calculated with physical/chemical contributions, - - - solubility calculated with physical contribution, ..... correlated solubility in pure CO<sub>2</sub>.

### *Polar dye with polar cosolvents*

The solubility of polar R60 in supercritical CO<sub>2</sub>-polar cosolvent mixture that was reported by Muthkumaran et al. (Figure 3(b))[6] was much higher than that of nonpolar B60. Compared to the pure CO<sub>2</sub>, 4.3mol% ethanol and acetone enhanced the solubility of R60 up to 160% at both 313.15 and 333.15 K. R60 has two polar functional groups (-OH and -NH<sub>2</sub>) and three slightly polar groups (two carbonyls and one ether) (Figure 1). The former can form hydrogen bonding with polar cosolvents. Since ethanol has a hydroxyl group, it can associate and form hydrogen bonds with all five polar groups (-OH, -NH<sub>2</sub>, =C=O, and -O-) in R60. Whereas the carbonyl group in acetone can form hydrogen bonds with -OH and -NH<sub>2</sub> groups in R60. Acetone is more polar than ethanol as its dipole moment is 2.87, while that of ethanol is 1.69 debye. Due to these stronger complexes, acetone has nearly the same solubility as ethanol in spite of its weaker hydrogen bonding capability.

$K_{CC}$  and  $K_{AC}$  were determined by eqs 6 to 9, assuming that acetone doesn't associate but ethanol associates infinitely. For 4.3% acetone or ethanol cosolvent, the solubilities of B60 and R60 were enhanced up to 80 and 160%, respectively. Therefore, we must count the chemical contribution to the solubility such as hydrogen bonding and charge-transfer complex formation between a polar cosolvent and a polar dye.

## CONCLUSIONS

A thermodynamic model developed as a function of density using Anderko's association and solvation (chemical) theory successfully described the cosolvent effect on the solubility of solid solute in SCF. The cosolvent effect on the solubility of nonpolar B60 was well explained using the Peng-Robinson EOS energy parameter obtained by correlating the solubility in pure CO<sub>2</sub>. For polar R60 the enhanced solubility was explained fairly well with both physical and chemical contributions to the solubility using the association and solvation constants that were estimated from the experimental solubility data. The predicted solubility using these constants and equations agreed well with the experimental solubility data for a different set of experiments. The solubility varied as a quadratic function of cosolvent concentration. For 4.3% acetone or ethanol cosolvent, the solubilities of B60 and R60 were enhanced up to 80 and 160%, respectively, above the solubility in the pure supercritical CO<sub>2</sub>.

## ACKNOWLEDGEMENTS

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