Measurement and correlation of solubility of anthraquinone derivatives in supercritical carbon dioxide

Measurement and correlation of solubility of anthraquinone derivatives in supercritical carbon dioxide

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Abstract

Solubility measurements of six anthraquinone derivatives in supercritical carbon dioxide (sc-CO_2) were carried out in a flow type apparatus at the temperature of (323.15, 353.15 and 383.15) K and over pressure ranges (12.5 to 25.0) MPa. Mole fraction solubility of six anthraquinone (1.1×10^{-7} to 351.25×10^{-7}) in the entire region of measurements. It was found that 1-aminoanthraquino is highest solubility. Four semiempirical density-based models were correlated, namely, Mendez - Santiago - Teja, Chrastil, Sung - Shim, and Kumar-Johnston. The solubilities of the dyes were analyzed also thermodynamically by the regular solution model with the Flory-Huggins theory and the Peng - Robinson equation of state modified by Stryjek and Vera (PRSV- EOS) with the conventional mixing rules. Good agreement between the experimental and calculated solubilities of dyestuff was obtained.

INTRODUCTION

Due to the increasing environmental concerns in conventional dyeing process that requires a large amount of water as a solvent, also generate much wastewater, therefore, new method of textile production have been intensively studied in the past years. Supercritical carbon dioxide can be used as a solvent to replace water, in addition, carbon dioxide has lower critical properties, both temperature and pressure, Tc (304.15 K) and Pc (7.383 MPa), respectively; it has inexpensive, nonflammable, and nontoxic. To develop and design the supercritical dyeing technology, solubility of dye, phase behaviour, should be known well. However, only a limited number of the experimental data for solubilities of dyestuffs in (sc-CO_2) is available in literature[1–9]. Two main group are commonly used as disperse dyes of polyester textiles, namely, anthraquinone and azo group. In particular, some researcher have been reported the solubility of anthraquinone dyestuffs in (sc-CO_2), both dynamic and static methods,with different model correlation, empirical, and semiempirical[1–9] , and also some author have been reported as review of solubility data of anthraquinone, method, deviations of the solubility data, experimental condition, of some researcher systematically[10,11]. In this work, we were measured six anthraquinone derivatives, because have a crucial important in polyester dyieng process. We apply four empirical equation to corelate the solubility; it is Mendez - Santiago - Teja[12], Chrastil[13], Chrastil modified by Sung and Shim[4], Kumar-Johnston[14] , the regular solution model with the Flory - Huggins theory, and the Peng - Robinson equation of state modified by Stryjek and Vera (PRSV-EOS)[15,16] with the conventional mixing rules.

EXPERIMENTAL

Materials

The chemical name, supplier, and purity of the chemicals used are presented in Table 1. These compounds were used directly without further purification.

Table 1: The chemical name, source, and purity of the chemicals.

Chemical name	Source	Mass fraction purity / %
1,4-diaminoanthraquinone (C.I. Disperse Violet 1)	Wako Pure Chemicals	> 0.96
1,4-bis(ethylamino)anthraquinone (C.I. Solvent Blue 59)	Aldrich	> 0.98
1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15)	Tokyo Chemical Industry CO.,LTD	> 0.98
1-hydroxy-4-nitroanthraquinone	Tokyo Chemical Industry CO.,LTD	> 0.97
1-aminoanthraquinone (Smoke Orange G)	Tokyo Chemical Industry CO.,LTD	> 98
1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin)	Tokyo Chemical Industry CO.,LTD	> 98
Carbon dioxide	Uno Sanso	$> 99,9$
Ethanol	Japan Alcohol Trading Company	> 99
Acetone	Wako Pure Chemicals	> 98

Apparatus and Procedures

The solubility measurement of two anthraquinones were performed using a flow-type apparatus. Previously, a detailed description of the apparatus is given elsewhere[1,17–19]. The flow diagram of the experimental setup is shown in Figure 1 . The equilibrium cell (150 mm long by 4.4 mm i.d.) used, is charged with ± 0.1 g of dye mixed with glass beads , were plugged with glass wool at both inlet and outlet sides of the equilibrium cell to make a uniform flow distribution of the supercritical fluids. The uncertainties of the temperature and pressure measurements were ± 0.1 K and ± 0.1 MPa, respectively. The experimental condition of this work, were described in detail in a previous work, hence a short description will be given here. After the carbon dioxide in the system reached the equilibrium pressure and temperature, a six-way valve (Rheodyne, model 7060) was turned to flow the carbon dioxide into the cell. The line from the exit of the oven to the back pressure regulator and cold trap was temperature controlled by a flexible heater to prevent it from clogging with dry ice or deposited dye in the flow lines. After every experimental run, the whole line of the apparatus was rinsed with appropriate solvent (e.g., ethanol). The solvent remaining in the line was completely removed by flowing fresh carbon dioxide through the line heated at 373.15

K with the oven and flexible heater. The solutes dissolved into supercritical carbon dioxide were collected by a two-step ice-cold trap filled with ethanol. Absorbance of the absorbed anthraquinone in solution was measured using a UV-visible spectrophotometer (Shimadzu, BioSpec-1600), the anthraquinone concentration was directly determined from the UV-absorbance of the dye. The solubility of the dyes was calculated from the anthraquinone concentration and volume of carbon dioxide measured by a wet gas meter (Shinagawa, W-NK-1B). Three replicates were performed at each experimental condition, and the solubility obtained is the average of these results

RESULTS AND DISCUSSION

Experimental Solubility Data

The solubilities of anthraquinone derivatives in supercritical carbon dioxide were measured at the temperature of (323.15, 353.15, and 383.15) K and over the pressure ranges (12.5 to 25.0) MPa. The solubility increases with the rise of temperature and pressure of CO_2 and the solubility of 1-aminoanthraquinone (Smoke Orange G) was highest . It was found that the amino group addition onto the anthraquinone molecule causes higher the solubility of the anthraquinone dye in (sc-CO_2). To our knowledge, the data solubility of these compounds has not been reported previously. Therefore, we cannot compare our results with the literature.

Empirical correlation of solubility data

In this work, the experimental results of the anthraquinone dyestuffs were correlated using four empirical density-based models;equation proposed by Mendez - Santiago - Teja[12], Chrastil[13], Sung and Shim[4], and Kumar-Johnston[14]. Mendez - Santiago - Teja[12] proposed a linear approximate expression on for the solubility of a solid solute in (sc- CO_2) at the system temperature T and pressure P on the basis of dilute solution theory as:

$$T\ln y_2 P = a_1 + a_2\rho + a_3 T, \tag{1}$$

Chrastil[13]was related the solubilities directly to the density of pure carbon dioxide, as form log-log relationship, as shown below;

$$\ln y_2 = k\ln\rho + \frac{a}{T} + b, \tag{2}$$

Sung and Shim[4] modified Charstil's equation into forms log-log relationship between solubility and density as;

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

Kumar-Johnston[14] proposed a equation for corelated the solubility of solid, as a function of density of pure carbon dioxide, and temperature, the semilog relantionship between solubility and density, as shown below:

$$\ln y_2 = A + \frac{B}{T} + C\rho, \tag{4}$$

where y_2 is the solubility of the solute in mole fraction, ρ is the density of sc-CO_2 calculated by the the NIST fluid property database and the parameters a_1 , a_2 , a_3, k, a, b, A, B, C, $A^{'}$, $B^{'}$, $C^{'}$ and $D^{'}$ of equation 1 to 4 were obtained from the experimental results by fminsearch function (MATLAB student version 2013) . The AARD is given by

$$\mathrm{AARD}(\%) = \frac{1}{ND}\sum_{i=1}^{n}\left|\left(\frac{y_{2,n}^{exp} - y_{2,n}^{cal}}{y_{2,n}^{exp}}\right|100, \right. \tag{5}$$

where ND is the number of experimental data. Figure 2 to 9 compare the experimental solubility data with those calculated from the equation 1 to 4.

Thermodynamic Framework

To correlate the solubility of two anthraquinone dyestuffs in sc-CO_2, within the terms of thermodynamic framework. The solution containing mixtures of polymer and solvent, Flory Huggins teory is most commonly used. In this study, we used the regular solution model coupled with the Flory - Huggins equation is reproduced by Iwai *et al.*[20]as

$$\ln y_2 = \frac{\Delta h_2^m}{RT}\left(\frac{T}{T_m} - 1\right) - \frac{v_2}{RT}(\delta_1 - \delta_2)^2 - \ln(v_2/v_1) - 1 + v_2/v_1, \tag{6}$$

where Δh_2^m and T_m are the melting enthalpy and melting temperature of solid component, respectively. v_1 and v_2 are the molar volume of sc-CO_2 and solid component. The solubility parameter of sc-CO_2 was calculated by the method of Giddings[21]

$$\delta_1/(\mathrm{MPa})^{0.5} = 2.0455 \times 1.25 P_c^{0.5}\left(\frac{\rho_R}{2.66}\right), \tag{7}$$

ρ_R (= ρ /ρ_c) is the reduced density of CO_2, ρ the density of sc-CO_2 calculated by Span wagner equation of state[22] , ρ_c and P_c are the critical density and pressure of CO_2. The solute solubility parameter was assumed to change as a function of the CO_2 density in the present work,

$$\delta_2 = a + b\rho_{CO_2}, \tag{8}$$

and

$$\delta_2 = a + b\rho_{CO_2}^c, \tag{9}$$

The parameters a, b, and c were obtained by minimizing the following objective function Q

$$\mathrm{Q} = \frac{1}{ND}\sum_{i=1}^{n}\left(\frac{y_{2,n}^{exp} - y_{2,n}^{cal}}{y_{2,n}^{exp}}\right)^2, \tag{10}$$

where *ND* is the number of experimental data. Figure 10 and 11 compare the experimental results with those calculated by equation 6.

Furthermore, we attempted to correlate the experimental results in terms of the equation of state applied in high-pressure phase equilibria. Assuming that no solvent dissolves in the solid phase, the solid solute is incompressible and its vapor pressure is very low, we can derive the following expression

$$y_2 = \frac{P_2^{subl} \exp\left[v_2^s (P - P_2^{subl})/RT\right]}{\phi_2{}^{SCF} P} \tag{11}$$

to calculate the solubilities of solid component in supercritical fluid. v_2^s is the molar volume of solid solute, P_2^{sub} the sublimation vapor pressure of solid component, and ϕ_2 is the fugacity coefficient of solid component in supercritical phase. The ϕ_2 can be calculated using an equation of state (EOS) by the thermodynamic relationship. The PRSV-EOS[16] with a modification of the attractive term of PR-EOS,[15,16] selected to calculate the solubility from a simplicity and accuracy view-point in representing the solid solubility in sc-CO_2, is expressed in the form of

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{12}$$

The conventional mixing rules of a and b for the binary solid and sc-CO_2 mixture are given by

$$a = \sum_i \sum_j x_i x_j a_{ij}, \tag{13}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \tag{14}$$

where the pure parameters a_{ii} and b_{ii} in PRSV-EOS were associated with the critical constants and the adjustable pure parameter

$$a_{ii} = \frac{0.45724 R^2 T_{C,i}^2}{P_{C,i}} \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_{C,i}}}\right)\right]^2, \tag{15}$$

$$b_{ii} = \frac{0.07780RT_{C,i}}{P_{C,i}}, \tag{16}$$

and

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R), \tag{17}$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3. \tag{18}$$

The reduced temperature T_R is given by T/T_c. The critical properties of anthraquinone derivatives were estimated by the Miller method,[23] the molar volume were done by the Fedors method,[24] and the acentric factor by the Edmister method[25]. The sublimation vapor pressure of the solid dyes was estimated by the method of Lee - Kesler[25]. The cross parameters a_{ij} and b_{ij} are given by the following van der Waals combining rules

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k_{ij}), \tag{19}$$

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj}), \tag{20}$$

where the binary interaction parameter k_{ij} was expressed by

$$k_{ij} = \alpha_{ij} + \beta_{ij}/T_R. \tag{21}$$

The coefficients α_{ij} and β_{ij} were obtained by minimizing the objective function given by equation 10. The adjustable parameter κ_1 of PRSV-EOS. κ_1 of CO_2 was set to zero. The correlated results for dye solubilities in sc-CO_2 using PRSV EOS with the optimum parameter are shown in Figure 12 for 1-aminoanthraquinone (Smoke Orange G) and Figure 13 for and 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin). Good agreement between the experimental and calculated solubilities of the dyes was obtained fitting the model to the experimental results.

CONCLUSIONS

The solubilities of six anthraquinone derivatives were measured over the pressure ranges (12.5 to 25.0) MPa and at the temperatures of (323.15, 353.15, and 383.15) K by a flow-type apparatus, and correlated successfully in terms of the density of carbon dioxide with the empirical equations of Mendez - Santiago - Teja,Chrastil, Sung - Shim, Kumar-Johnston, and also correlated satisfactorily with Flory - Huggins theory ,and the Peng - Robinson equation of state modified by Stryjek and Vera (PRSV EOS) with the conventional mixing rules. Good agreement between the experimental and calculated solubility of the dyestuffs was obtained.

Acknowledgement

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FIGURE

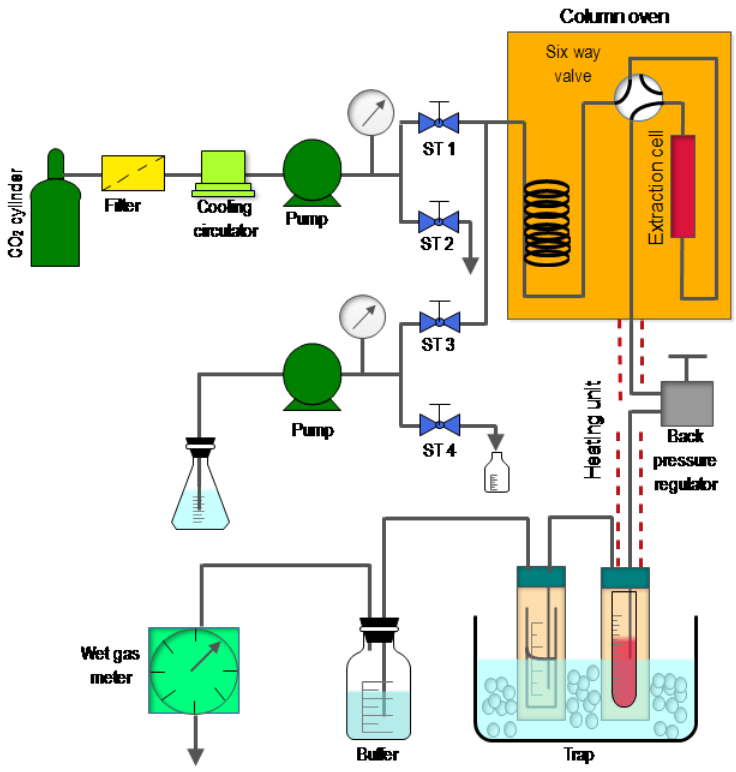

Figure 1: The flow diagram of experimental apparatus.

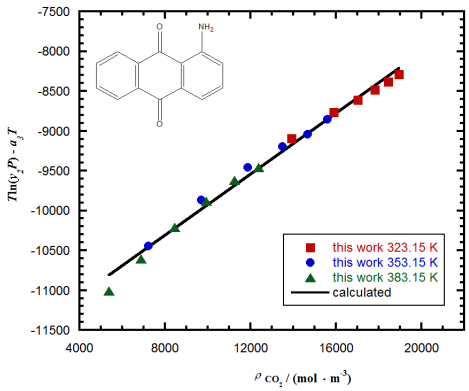

Figure 2: Plot of ($Tln(y_2P)$-a_3T) against density ρ/(mol·m^{-3}) to correlate results for 1-aminoanthraquinone (Smoke Orange G) from Mendez-Santiago-Teja model.

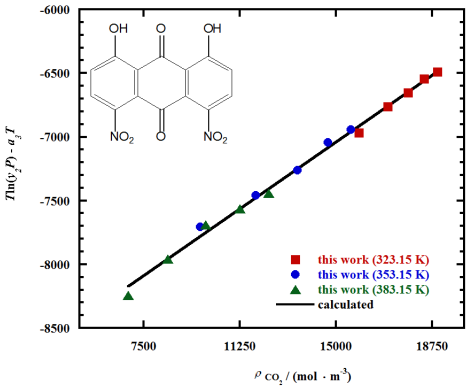

Figure 3: Plot of ($Tln(y_2P)$-a_3T) against density ρ/(mol·m^{-3}) to correlate results for 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin) from Mendez-Santiago-Teja model.

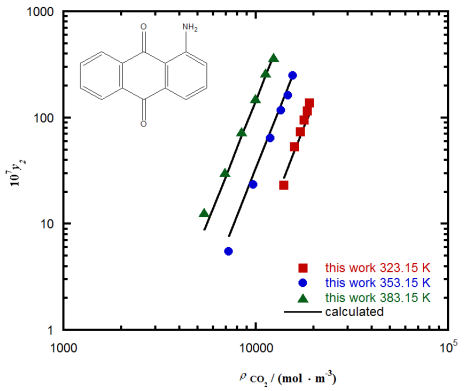

Figure 4: Plot of mol fraction $10^7 y_2$ against density $\rho/(\text{mol}\cdot\text{m}^{-3})$ to correlate results for 1-aminoanthraquinone (Smoke Orange G) from Chrastil model.

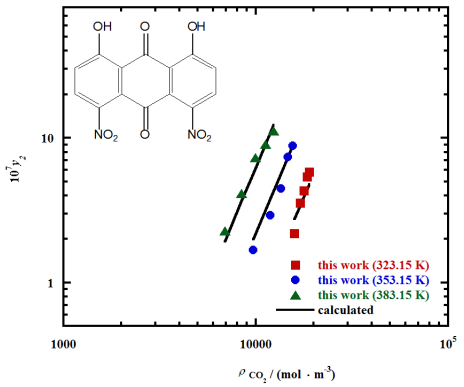

Figure 5: Plot of mol fraction $10^7 y_2$ against density $\rho/(\text{mol}\cdot\text{m}^{-3})$ to correlate results for 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin) from Chrastil model.

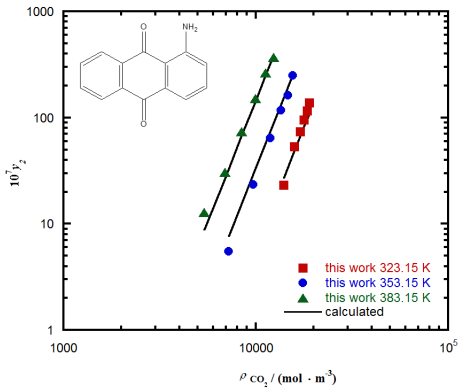

Figure 6: Plot of mol fraction $10^7 y_2$ against density $\rho/(\text{mol}\cdot\text{m}^{-3})$ to correlate results for 1-aminoanthraquinone (Smoke Orange G) from Sung-Shim model.

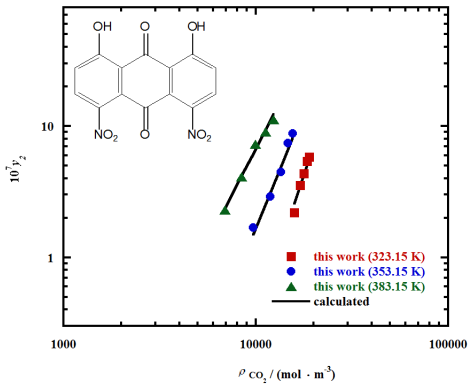

Figure 7: Plot of mol fraction $10^7 y_2$ against density $\rho/(\text{mol}\cdot\text{m}^{-3})$ to correlate results for 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin) from from Sung-Shim model.

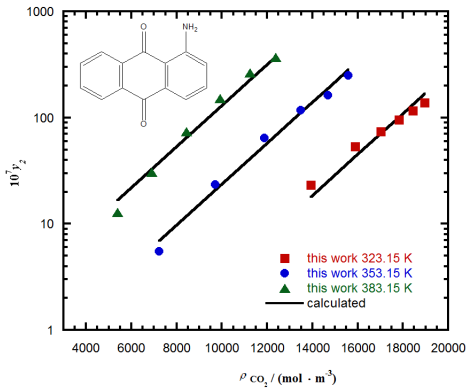

Figure 8: Plot of mol fraction $10^7 y_2$ against density $\rho/(\text{mol}\cdot\text{m}^{-3})$ to correlate results for 1-aminoanthraquinone (Smoke Orange G) from Kumar-Johnston model.

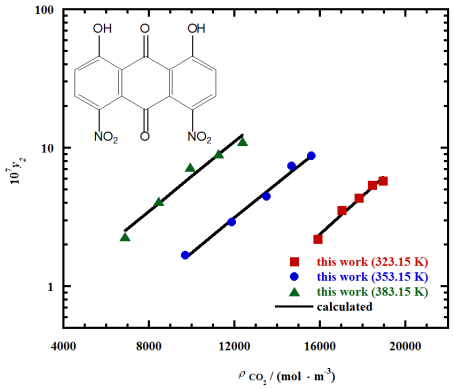

Figure 9: Plot of mol fraction $10^7 y_2$ against density $\rho/(\text{mol}\cdot\text{m}^{-3})$ to correlate results for 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin) from from Kumar-Johnston model.

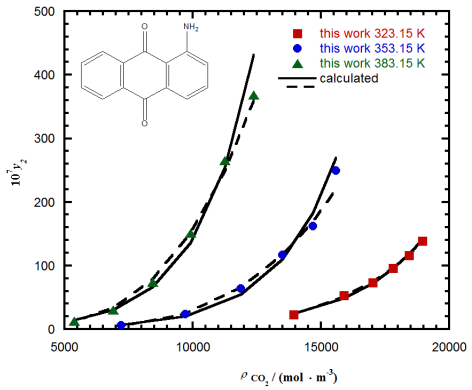

Figure 10: Plot of mol fraction $10^7 y_2$ against density ρ/(mol·m^{-3}) to correlate results for 1-aminoanthraquinone (Smoke Orange G) from regular solution model with Flory-Huggins equation.

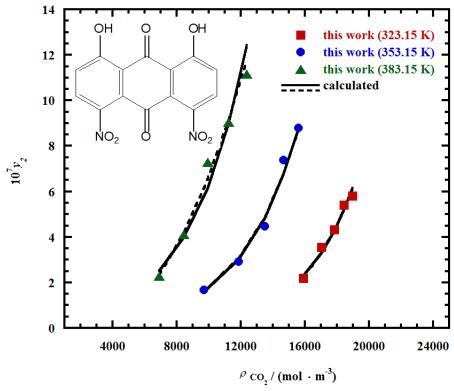

Figure 11: Plot of mol fraction $10^7 y_2$ against density ρ/(mol·m^{-3}) to correlate results for 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin) from regular solution model with Flory-Huggins equation.

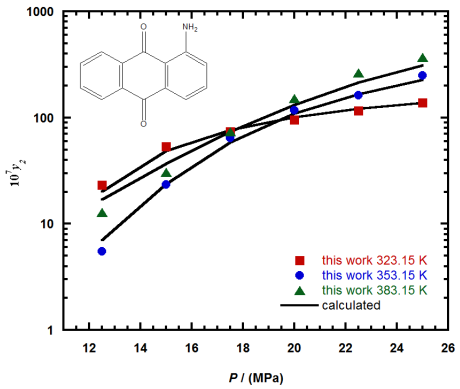

Figure 12: Plot of mol fraction $10^7 y_2$ against Pressure P/MPa to correlate results for 1-aminoanthraquinone (Smoke Orange G) from PRSV equation of state.

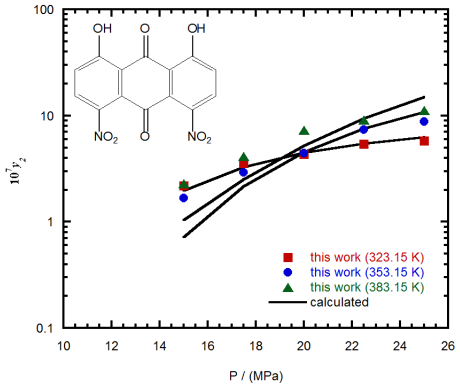

Figure 13: Plot of mol fraction $10^7 y_2$ against Pressure P/MPa to correlate results for 1,8-dihydroxy-4,5-dinitroanthraquinone (4,5-dinitrochrysazin) from PRSV equation of state.

平成 26 年 8 月 4 日

学位論文審査報告書（甲）

1．学位論文題目（外国語の場合は和訳を付けること。）

Measurement and correlation of solubility of anthraquinone derivatives in supercritical carbon dioxide （超臨界二酸化炭素中でのアントラキノン誘導体の溶解度測定および相関）

2．論文提出者 (1) 所　　属 物質科学専攻

(2) 氏（ふり）　名（がな） Ratna Surya Alwi（らとな するや あるうぃ）

3．審査結果の要旨（600～650 字）

提出された学位論文に対し、各審査員による個別審査と指導を行うとともに、平成 26 年 7 月 11 日に第 1 回論文審査委員会を開催し、同 8 月 4 日開催の口頭発表の結果をふまえ、同日開催の第 2 回論文審査委員会にて協議し、以下のとおり判定した。

超臨界染色プロセス設計・開発には染料の溶解度などの基礎物性データが必要となる。提出者は超臨界二酸化炭素中でのアントラキノン系誘導体の溶解度を温度範囲（323～383K）、圧力範囲(12.5～25MPa)で測定し、経験式および熱力学モデルによる実験結果の相関法について検討した。なかでも置換基（アミノ基、ニトロ基、水酸基、アルキル基）を有する 6 種類のアントラキノン誘導体の超臨界二酸化炭素中での溶解度データから、溶解度の置換基による影響を明らかにした。また、新たに改良した正則溶液モデルにより、実験値を正確に相関する方法を提案した。以上の成果は超臨界流体の基礎物性の解明およびその利用技術に新たな知見を与えるものである。

よって、本論文は博士（工学）の学位に値するものと判定する。

4．審査結果 (1) 判　　定（いずれかに○印） （合　格） 不合格

(2) 授与学位 博　士（工　学）