Quinacridone Solubility in Hot-Compressed Water

Kiwamu Sue,*,†,‡ Toshihiko Usami,‡ Kunio Arai,‡ Hitoshi Kasai,§ Hachiro Nakanishi,§ and Toshihiko Hiaki†

Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, 1-2-1 Izumi-cho, Narashino, Chiba, 275-8575, Japan, Graduate School of Environmental Studies, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai, 980-8579, Japan, and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Sendai, 980-8577, Japan

The solubility of quinacridone in hot-compressed water was measured for the first time at temperatures from (453.4 to 592.9) K and at a pressure of 24 MPa with a flow-type apparatus. The solubility varied from 1.07×10^{-5} mol·kg^{-1} at 453.4 K to 5.89×10^{-3} mol·kg^{-1} at 592.9 K. Dissolution equilibria of quinacridone were analyzed by a simple thermodynamic model on the basis of the measured solubility.

Introduction

Nanocrystals of quinacridone and its derivatives are attracting much attention because of promising application for electroluminescent materials and red pigments.[1] Among several fabrication methods of these organic nanocrystals, the hot-compressed water (HCW) recrystallization method is one of the effective and environmentally friendly techniques for preparation of organic nanocrystals such as phthalocyanine, quinacridone, and fullerene C60.[2−4] In this method, HCW is used as an extraction solvent because HCW has a low dielectric constant (about 5 to 50) compared with water at room temperature (around 80)[5] and at these conditions it behaves like a weakly polar organic solvent and also shows higher solubility to organic compounds. With this method, organic nanocrystals successfully precipitate by mixing the extracted organic aqueous solution with cooling water without any organic solvents.[2] For this application, solubility of quinacridone at these conditions is essential to clarify the key factor of controlling the crystal size and form.

Some researchers have proposed flow-through methods for measuring accurate metal oxide solubility in HCW.[6,7] A flow-through-type apparatus is used with an extraction cell, and the solubility is determined on the basis of the molalities in recovered solution. For the case in which the solubility at room temperature is lower than that at higher temperature, the metal oxide has a tendency to recrystallize within the cool down heat exchanger and the typical result is plugging of the lines and termination of the experiment in higher-temperature conditions. To ensure that metal oxides do not precipitate in the cool down portion, mixing of the metal oxide solution with acid or base at the given conditions following the extraction has been used. This method is effective to measure the solubility of chemically stable compounds. For the case of organic solids, one idea is to mix the aqueous solution of organics with good solvents such as *N*-methylpyrrolidone and dimethylsulfoxide. However, there exists the possibility of decomposition of the solvents and also reaction of organic solids with the solvents at high-temperature conditions. Therefore, the method is difficult to apply.

* Corresponding author. TEL/FAX: +81-47-474-9682/9684. E-mail: k5sue@ cit.nihon-u.ac.jp.
† Nihon University.
‡ Graduate School of Environmental Studies, Tohoku University.
§ Institute of Multidisciplinary Research for Advanced Materials, Tohoku University.

In this work, we describe an experimental system that is suitable for measuring solubilities of organic crystals in HCW and report on quinacridone solubility at a pressure of 24 MPa and temperatures ranging from (453.4 to 592.9) K. Dissolution equilibria were analyzed by a simple thermodynamic model on the basis of the measured solubility. Values for the equilibrium constant and the standard enthalpy and heat capacity of the dissolution reaction at reference conditions were evaluated from the temperature dependence of the equilibrium constant.

Experimental Section

A schematic diagram of the experimental apparatus is shown in Figure 1. It consisted of two feed systems, pressure and temperature measurement and control systems, an effluent collection, an electric furnace, a micromixing unit, and an extraction cell. A stainless steel (SUS316) tube (1.58 mm o.d., 0.59 mm i.d.) and union tee (1.3 mm i.d.) were used for high-pressure sections except for the micromixing unit. The micromixing unit was composed of a union tee (0.3 mm i.d.), a SUS316 tube (1.58 mm o.d., 0.13 mm i.d., 50 mm length), and a micro heater. The micro heater and the tube having the smaller inner diameter were used to reduce precipitation and plugging in the tube between the extraction cell and the mixing tee because of decreasing temperature and flow velocity. The extraction cell (manufactured by ACRAFT) was made of SUS316 with dimensions of 70 mm i.d. and 122 mm height (470 cm^3 volume) and was set up horizontally. The electromagnetic induction rotating stirrer, with a maximum rotation speed of 1500 rpm, was placed at the bottom of the cell. The solution temperature in the cell was controlled by a sheathed heater located along the inner wall. The quinacridone crystal (*β*-form, approximately 25 g, purchased from Tokyo Kasei Kogyo, purity >98 %) was placed in the cell.

Distilled and deionized water for the extraction was fed at a flow rate of 10 g·min^{-1} by high-performance liquid chromatography (HPLC) pump 1. From another line, distilled and deionized water for cooling was fed at a flow rate of 20 g·min^{-1} by HPLC pump 2. The water for extraction was heated to the extraction temperature in the SUS316 tube with the electric furnace and then flowed into the cell. At the exit of the cell, an inline filter, housing 0.5 μm of the sintered stainless steel element, was set to retain quinacridone crystals. The residence time of water for extraction in the cell was about 47 min. The
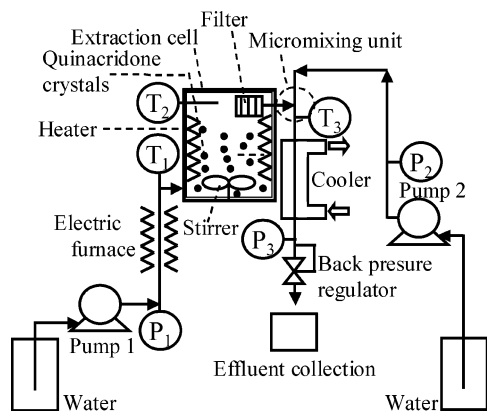
Figure 1. Schematic diagram of the experimental setup for solubility measurement.

rotation speed of the electromagnetic stirrer was set to 0−1000 rpm. The high-temperature quinacridone aqueous solution flowing through the filter was mixed with cooling water in the micromixing unit and then cooled to ambient temperature by a cool down heat exchanger. System pressure was controlled by a back-pressure regulator (model 26-1700, TESCOM). All measurements were carried out at temperatures from (453 to 593) K and a pressure of 24 MPa, having the uncertainties of temperature (±0.1 K) and pressure (±0.1 MPa). After depressurization, precipitated crystals were collected in a glass flask as a slurry solution. After each experiment, no solid residue was observed in the tube and union placed from the micromixing unit to the back-pressure regulator. This result clearly shows that all the precipitates are successively collected in the flask. The effluent solution was weighed with an analytical balance within the uncertainties of ±0.1 mg. Solids in the effluent solution were filtered by a membrane filter, washed with pure water, dried at 373 K in an oven for 24 h for removal of water in resultant solids, and then weighed with the analytical balance. After that, quinacridone molality in water, m, was determined by the following relation:

$$m = \frac{W_Q/M_{W,Q}}{W_{H_2O}} \qquad (1)$$

where $M_{W,QA}$, W_{QA}, and W_{H_2O} are the molecular weight of quinacridone, 312.327×10^{-3} kg·mol^{-1}, the mass of solid quinacridone, and the mass of water delivered by pump 1, respectively. The crystal size and structure of the solids in the slurry solution were analyzed by transmission electron microscopy (TEM, Carl Zeiss, LEO 922 OMEGA) and UV/vis spectrophotometry (V-570, JASCO), respectively. The molality of total organic carbon in solution after the filtration was analyzed by the total organic carbon analyzer (TOC-V CPH/CPN, Shimazu). On the basis of the molality, the molality of the dissolved quinacridone molecule was estimated and the value was lower than 10^{-7} mol·kg^{-1} in each experiment.

Results and Discussion

TEM images of raw material and solid in the effluent obtained after exposure to 573 K are shown in Figure 2. The average particle diameter of the raw material and the obtained solid are 1.8 μm and 65 nm, respectively. This indicates that larger crystals of the raw material dissolve in HCW, and the rapid cooling in the micromixing unit promises the formation of smaller crystals and also the prevention of plugging in the experimental line. Typical results of absorption spectra of a
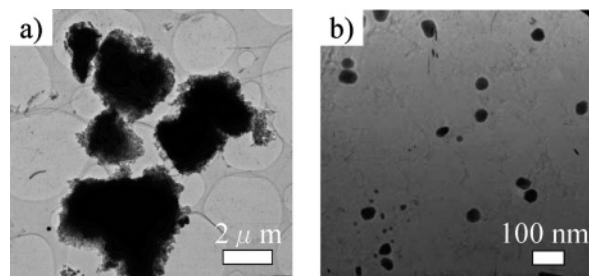

Figure 2. TEM images of (a) raw material and (b) crystals obtained from the effluent after exposure to 573 K.
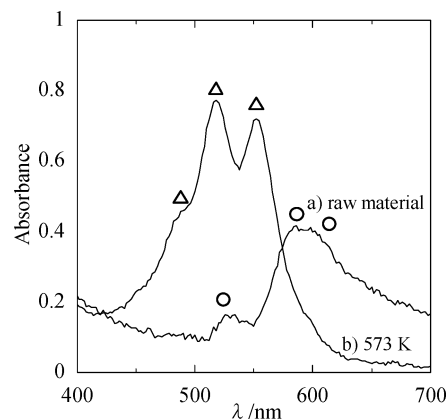

Figure 3. Absorption spectra of raw material and crystals obtained from the effluent after exposure to 573 K: $\bigcirc$, β-form; $\triangle$, α-form.
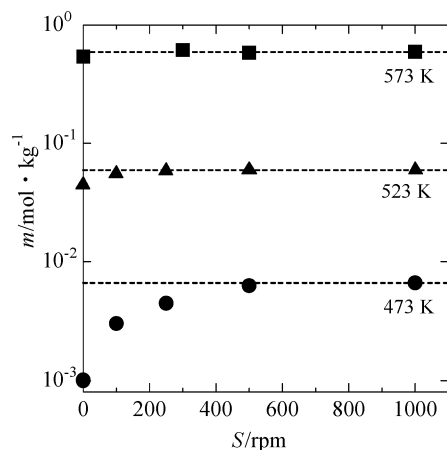

Figure 4. Quinacridone molality m as a function of rotation speed S.

quinacridone crystal dispersion liquid obtained after exposure to 573 K are shown in Figure 3. The absorption spectrum is assigned to the single phase of the meta-stable α-form of the quinacridone crystal.[8] No significant difference for the absorption spectra was observed at other temperatures. The metal-stable α-form nanocrystals are obtained in effluent due to the rapid quench of the extracted solution for the collection as precipitates in solution. The measured value in this work, however, is the molality of stable β-form crystals.

Especially for unknown solubilities, the method depends on the solution becoming saturated with solid solute during the extraction time in the cell. To ascertain that the solutions were saturated, we measured the variation of quinacridone molality in the recovered solution with rotation speed. Figure 4 shows the relationship between the quinacridone molality and the rotation speed, S/rpm, for the quinacridone + water system at temperatures from (473 to 573) K. As shown in Figure 4, it was found that the solution required a rotation speed of at least

**Table 1. Quinacridone Solubility in Hot-Compressed Water**[a]

T/K	t/min	10^3 s/mol·kg^{-1}	T/K	t/min	10^3 s/mol·kg^{-1}
453.4	15	0.0112	549.0	15	0.5408
	45	0.0118		45	0.5392
	75	0.0102		75	0.5241
	105	0.0096		105	0.5337
	135	0.0106		135	0.5373
	av	0.0107 (±0.0009)		av	0.5350 (±0.0067)
462.9	15	0.0163	563.5	15	1.1277
	45	0.0144		45	1.0992
	75	0.0170		75	1.1475
	105	0.0160		105	1.1168
	135	0.0157		135	1.0950
	av	0.0159 (±0.0010)		av	1.1171 (±0.0215)
473.9	15	0.0215	573.0	15	1.9595
	45	0.0215		45	1.9413
	75	0.0224		75	1.8676
	105	0.0202		105	1.8795
	135	0.0215		135	1.8465
	av	0.0214 (±0.0010)		av	1.8990 (±0.0170)
498.6	15	0.0439	583.5	15	3.0520
	45	0.0480		45	3.0337
	75	0.0522		75	3.0379
	105	0.0503		105	3.0504
	135	0.0515		135	3.0309
	av	0.0493 (±0.0035)		av	3.0398 (±0.0099)
508.2	15	0.0964	592.9	15	6.0659
	45	0.0954		45	5.7214
	75	0.0897		75	5.7739
	105	0.0909		105	5.9686
	135	0.0945		135	5.9080
	av	0.0932 (±0.0029)		av	5.8876 (±0.1409)
522.5	10	0.2465			
	30	0.2401			
	50	0.2337			
	70	0.2369			
	90	0.2449			
	av	0.2404 (±0.0054)			

[a] Values in parentheses are SDs in estimations of the average value.

500 rpm to become saturated with quinacridone. Therefore, we set the rotation speed to 1000 rpm for each set of experimental data at given temperatures.

The experimental results of quinacridone solubility on each extraction time, t/min, in HCW are shown in Table 1 together with the average value at given temperatures and its standard deviation. The measured solubility drastically increased with increasing temperature. Further, for confirming the achievement to equilibrium solubility, quinacridone molality was measured at a low flow rate of (2.0 and 5.0) g·min^{-1}, 573 K, 24 MPa, and 1000 rpm and the values were (1.8523 and 1.9474) × 10^{-3} mol·kg^{-1}, respectively. In addition, quinacridone solubility was also measured four times with the recently proposed static method[9] at 573 K and 24 MPa for 120 min and the value was 1.95 ± 0.11 × 10^{-3} mol·kg^{-1}. These values show good agreement with the data, as shown in Table 1.

General dissolution reactions between quinacridone and HCW and the equilibrium constant K are expressed as follows

$$\text{quinacridone(s)} + n\text{H}_2\text{O} = \text{quinacridone·}n\text{H}_2\text{O(aq)} \quad (2)$$
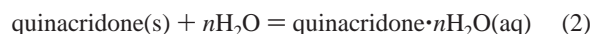
$$K = \frac{a_{\text{quinacridone·}n\text{H}_2\text{O(aq)}}}{a_{\text{quinacridone(s)}} \times a_{\text{H}_2\text{O}}^n} \quad (3)$$

where n and a are the hydration number and the thermodynamic activity, respectively. Equations 2 and 3 are based on the assumption that the molality of quinacridone is low. Furthermore, in dilute solutions, the molality does not differ from the thermodynamic activities. In the usual manner, the thermodynamic activities of a pure solid and water are taken to be unity.
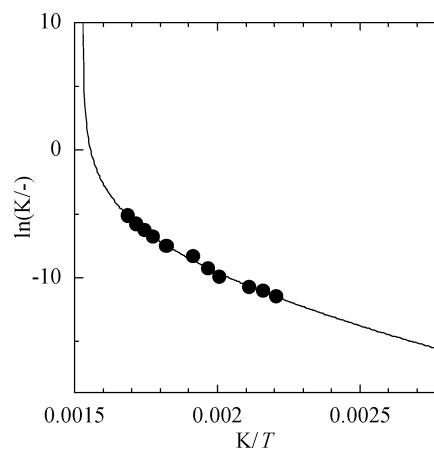

Figure 5. Comparison between experimentally determined and correlated ln K for quinacridone dissolution at 24 MPa.

For the reaction, the equilibrium constant can be changed as follows

$$\ln K = \ln[\text{quinacridone·}n\text{H}_2\text{O(aq)}] = \ln s \quad (4)$$

where s/mol·kg^{-1} is quinacridone solubility.

In this work, we analyze the experimental ln K data for the quinacridone dissolution reaction at given conditions using the following simplified density model by Anderson et al.[10]

$$\ln K = \ln K_r - \frac{\Delta H_r^0}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) + \frac{\Delta C_{Pr}^0}{RT_r(\partial\alpha/\partial T)_{Pr}}\left(\frac{1}{T}\ln\frac{\rho}{\rho_r} - \frac{\alpha_r}{T}(T - T_r)\right) \quad (5)$$

where ln(K/−), ΔH^0/J·mol^{-1}, and ΔC_P^0/J·mol^{-1}·K^{-1} denote the equilibrium constant, the standard enthalpy, and the heat capacity of the dissolution reaction. R is the gas constant 8.314 J·mol^{-1}·K^{-1}. T/K, ρ/g·cm^{-3}, and α/K^{-1} stand for absolute temperature, water density, and thermal expansivity, respectively. ρ and α were estimated by formulations of Wagner and Pruss.[11] The subscript r denotes the reference state of 298.15 K and 0.1 MPa. In this work, ln K_r, ΔH_r^0, and ΔC_{Pr}^0 are treated as fitting parameters. The determined parameters were −18.36 ± 0.55, (37.9 ± 3.7) kJ·mol^{-1}, and (286.0 ± 11.0) J·mol^{-1}·K^{-1}, respectively. Estimated uncertainties are from propagation of the experimental uncertainties. The standard deviation of the regression in ln K was 0.14. Comparisons between experimentally determined and correlated ln K values for the quinacridone dissolution reaction are shown in Figure 5. The model could describe well the temperature dependence of ln K.

Conclusions

A new technique was proposed for measuring the solubility of solids in hot-compressed water. New data were reported for quinacridone red pigment in hot-compressed water. A simple thermodynamic model could correlate the data as a function of temperature and water density.

Literature Cited

(1) Lincke, G. A. Review of Thirty Years of Research on Quinacridones. X-ray Crystallography and Crystal Engineering. *Dyes Pigm.* **2000**, *44*, 101−122.

(2) Komai, Y.; Kasai, H.; Hirakoso, H.; Hakuta, Y.; Katagi, H.; Okada, S.: Oikawa, H.; Adschiri, T.; Inomata, H.; Arai, K.; Nakanishi, H. Preparation of Organic Microcrystals Using Supercritical Fluid Crystallization Method. *Jpn. J. Appl. Phys.* **1999**, *38*, L81−L83.

(3) Li, B.; Kasai, H.; Oikawa, H.; Okada, S.; Arai, K.; Nakanishi, H. Fabrication and Characterization of Quinacridones Nanocrystals by High-Temperature and High-Pressure Crystallization Method. *Int. J. Nanosci.* **2002**, *1*, 587−592.

(4) Li, B.; Kasai, H.; Oikawa, H.; Okada, S.; Arai, K.; Nakanishi, H. Monodispersed Quinacridone Nanocrystals Prepared by a High-Temperature and High-Pressure Liquid Crystallization Method. *J. Nanosci. Nanotechnol.* **2003**, *3*, 365−367.

(5) Fernández, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Sengers, J. M. H. L.; Williams, R. C. A Formulation for the Static Permittivity of Water and Steam at Temperatures from 238 K to 873 K at Pressures up to 1200 MPa, Including Derivatives and Debye−Hückel Coefficient. *J. Chem. Eng. Ref. Data* **1997**, *26*, 1125−1166.

(6) Sue, K.; Hakuta, Y.; Smith, R. L., Jr.; Adschiri, T.; Arai, K. Solubility of Lead(II) Oxide and Copper(II) Oxide in Subcritical and Supercritical Water. *J. Chem. Eng. Data* **1999**, *44* (6), 1422−1426.

(7) Bénézeth, P.; Palmer, D. A.; Wesolowski, D. J.; Xiao, C. New Measurements of the Solubility of Zinc Oxide from 150 to 350 °C. *J. Solution Chem.* **2002**, *31* (12), 947−973.

(8) Filho, D. S.; Oliveira, C. M. F. Crystalline Modifications of Linear Trans-Quinacridone Pigments. *J. Mater. Sci.* **1992**, *27*, 5101−5107.

(9) Sue, K.; Mizutani, T.; Usami, T.; Arai, K.; Kasai, H.; Nakanishi, H. Titanyl Phthalocyanine Solubility in Supercritical Acetone. *J. Supercrit. Fluids* **2004**, *30* (3), 281−285.

(10) Anderson, G. M.; Castet, S.; Schott, J.; Mesmer, R. E. The Density Model for Estimation of Thermodynamic Parameters of Reactions at High Temperatures and Pressures. *Geochim. Cosmochim. Acta* **1991**, *55*, 1769−1779.

(11) Wagner, W.; Purss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.