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Solubility and growth rate of reactive blue49 and black8 dyes in salting-out system

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Abstract−Reactive dyeing is one of most widely used methods for the coloration of cellulosic fibers. Reactive dyes have a low utilization degree compared to other types of dyestuff, since the functional group also bonds to water, creating hydrolysis. Salting out crystallization process was used to obtain dye crystals from solution. Physical properties and growth rate were measured for the design of the crystallization process. Density of RB8 crystal was 1.92 g/cm^3 and that of RB49 was 1.26 g/cm^3. Density of dye solution was linearly decreased with rise in temperature. Saturation solubility to the water was constant over room temperature. Solubility of dye solution was decreased by higher temperature and higher KCl concentration. The growth rate of RB8 was $0.964\times10^{-06}\Delta C^{1.041}$ and that of RB49 was $2.922\times10^{-06}\Delta C^{2.236}$ respectively.

Key words: Solubility, Dye, Salting-out Crystallization, Density, Growth Rate

INTRODUCTION

Crystallization from solution is an important separation and purification technique used to produce a variety of materials for the chemical, pharmaceutical and electronic industries [1-4]. Many crystallization processes have been adopted such as evaporating crystallization, cooling crystallization, salting-out crystallization, etc. in dye industry. Reactive dyes were first developed by ICI in the 1950s, and were of particular importance in dyeing cellulosic fibers such as cotton. They gave fast dyeing on cotton by a more convenient process and at a lower cost than had previously been possible. Reactive dyes are the most common dyes used due to their advantages, such as bright colors, excellent color fastness and ease of application [6-8]. Reactive dyes are normally obtained by salting-out crystallization or spray drying after synthesis in industry. In salting out crystallization, diluent reduces the solubility of the solute, thus generating the required supersaturation. Salting-out crystallization is useful for highly heat sensitive materials, so this process is suitable to produce dye crystals efficiently. The physical property of the final product is very important for researching its operating conditions. Solubility is one of the most fundamental physiochemical properties that is particularly useful to a wide variety of applications important to the biological, chemical, pharmaceutical and dye industries [10]. Accurate solubility data is needed for process and product design including production and purification of pharmaceutical compounds, formulation, controlled drug delivery systems, bio-separations, food processing, chemical reaction systems and precipitation/crystallization processes. Several groups [11-19] reported on the crystallization kinetics and habit change in batch and MSMPR crystallization systems. The kinetics of crystal growth is important in the design and development of crystallization processes. A number of crystal growth theories have been developed and are reviewed in the literature [9]. In this research, the density of dye crystal and density of dye solution, solubility of dye solution and growth rate of dye crystal were investigated.

CRYSTAL GROWTH RATE

The analysis and development of industrial crystallization processes requires knowledge of the kinetics of the crystal growth process. For engineering purposes in crystallizer design and assessment, the simple empirical power-law relationship expressing specific rate of mass deposition purposes is given by

$$R=\frac{1}{A_T}\frac{dW}{dt}=k_G\Delta c^g \tag{1}$$

It can be expressed for a different basis such as mass of solid rather than crystal surface area. It is also convenient to express the overall linear growth rate instead of the mass deposition for an ensemble with constant population of crystals as

$$G\equiv\frac{dL}{dt}=k_g\Delta c^g \tag{2}$$

where G is the size independent crystal growth rate and kg depends on temperature, crystal size and so on.

EXPERIMENTAL

1. Materials

The RB8 (reactive black 8) and RB49 (reactive blue 49), which are popular reactive dyes, were selected by means of representative dye for this research. They were provided by Ohyoung Co. Their chemical structures are shown in Fig. 1. Those are structurally azo-type dye and prepared via 4 step reactions. The chloro group of reactive dye reacts chemically with the fibers and becomes fixed to it by covalent bonds during the dyeing process. KCl (DUKSAN, 99.0%) was used as salting out agent.

2. Apparatus

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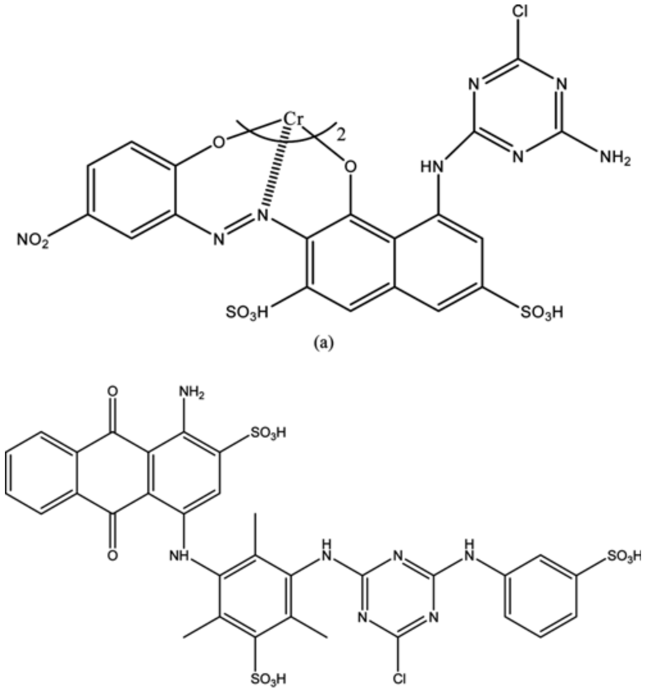
[‡]This article is dedicated to Professor Chul Soo Lee in commemoration of his retirement from Department of Chemical and Biological Engineering of Korea University.



(a)

(b)

Fig. 1. Structure of (a) Reactive Black 8 and (b) Reactive Blue 49.

The growth rate experimental apparatus used in this research is shown Fig. 2. It consisted of crystallizer, constant temperature bath and chambers. The crystallizer's diameter was 10 cm, and 14 cm high. Its volume was 1,000 cm^3. For the perfect mixing, 1 cm wide baffles were attached to the wall, and it was agitated by a mechanical stirrer (RZR-2020) with three blade marine propeller. To keep a constant temperature during experiments, a constant temperature bath was used (Brookfield TC-101D-230). Each chamber is made of plastic and it is 4 cm wide, 4 cm long and 1 cm high. Its volume is 16 cm^3. To flow the solution into chamber, 0.3 cm inner diameter tube was put into the chamber wall. Micro tubing pump (EYELA) was used for solution pumping. 10 μm dye crystal was attached by glue at the end of 1.1 cm long needle. It was immersed in solution in the chamber during experiments.

3. Methods

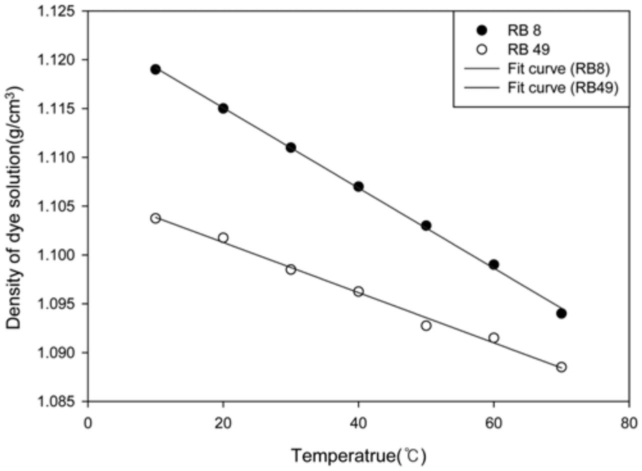


Fig. 3. Density of 20 wt% RB8 and RB49 solution.

3-1. Physical Property

For physical properties experiments, the density of RB8 and RB49 powder was measured by using a 25 ml pycnometer. The density of 20 wt% solution of RB8 and RB49 was also measured by using a specific gravity balance in the temperature range between 10 and 70 °C. The solubility of RB8 and RB49 in 100 ml distilled water was determined from 10 to 60 °C in 10 °C steps. The temperature of mixture was controlled and continuously stirred in a mechanically shaken incubator (HB-201SF) for 24 hours. The solution was filtered by a 0.45 μm membrane to separate solid which was not dissolved in distilled water and then the separated solid was weighed after being dried at least 24 hours at 80 °C in a dry oven (Johnsam). The solubility of RB8 and RB49 in water-potassium chloride mixture was also measured at 25, 30 and 35 °C. After the mixture was filtered, weak solution was analyzed with a UV/VIS Spectrometer (Jasco V-550) to evaluate the solubility of dyes in water-potassium chloride.

3-2. Growth Rate

The growth rate of dye crystals (RB8 and RB 49) was determined from aqueous solution by salting out technique. The dye solution (20 wt%) was used. The temperature of the solution was kept constant at 25 °C by using constant temperature bath. Potassium chloride (15 wt%), which was the salting-out agent, was added into

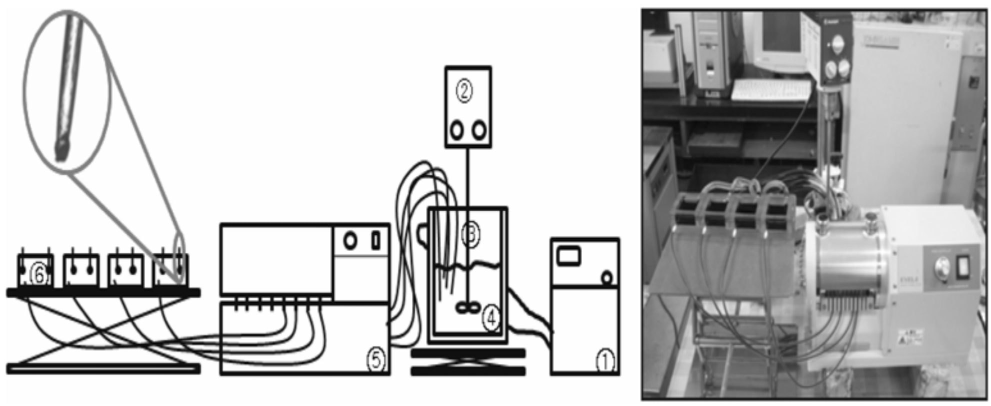


Fig. 2. Schematic apparatus (① Heating bath, ② Agitator, ③ Propeller, ④ Double jacket, ⑤ Micro Tubing Pump, ⑥ 16 ml reactor).

the dye solution. Micro tubing pump was used to carry solution from crystallizer to 16 ml chamber slowly, approximately 2.7 ml/min. The concentration of solution was determined by periodically sampling the solution from the crystallizer with a micro pipet, and was analyzed by UV/VIS spectrometer. Dye crystal, which was attached on a wire, was taken out from chamber every hour and the mass of dye crystal was weighed. To evaluate the growth rate, G, the weight change of solid phase was divided by density of dye crystals to transform into volume change. Its value was extracted cubic root and divided by time. Concentration change was obtained during experiment by sampling of the solution and from solubility curve in water-potassium chloride mixture. Crystal growth parameters, k_g and g, were determined from log-log plot growth rate versus concentration change.

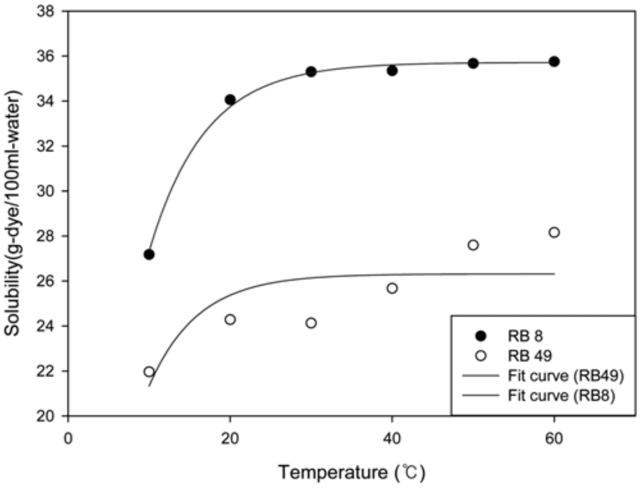
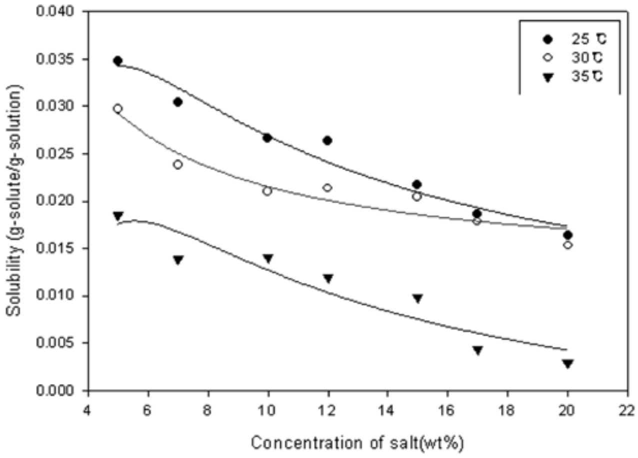


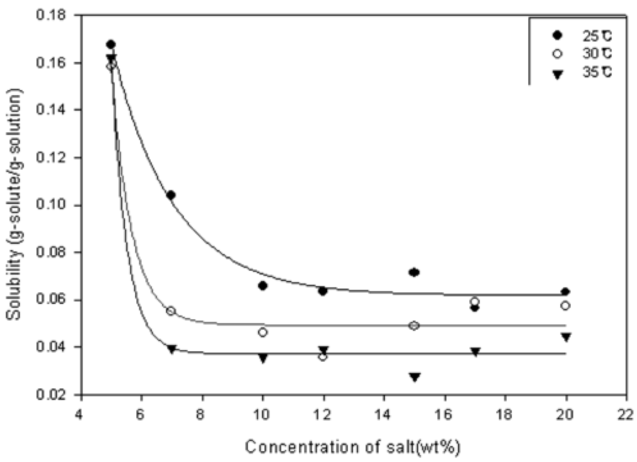
Fig. 4. Solubility of RB8 and RB49 in water.

RESULTS AND DISCUSSION

The crystal density of RB8 and RB49 was about 1.92 g/cm^3 and 1.26 g/cm^3, respectively. Normal hexane was used by means of solvent to measure the density of dye crystals, because the dyes are well soluble in water. Fig. 3 shows the density of 20 wt% RB8 and RB49 solution in water in the temperature between 10 ℃ and 70 ℃. There is a linear decrease in the density of RB8 and RB49 with rise in temperature, but the temperature dependency of the solution density was small. The saturation solubility of RB8 and RB49 is shown in Fig. 4. The saturation solubility of RB8 reaches a plateau over

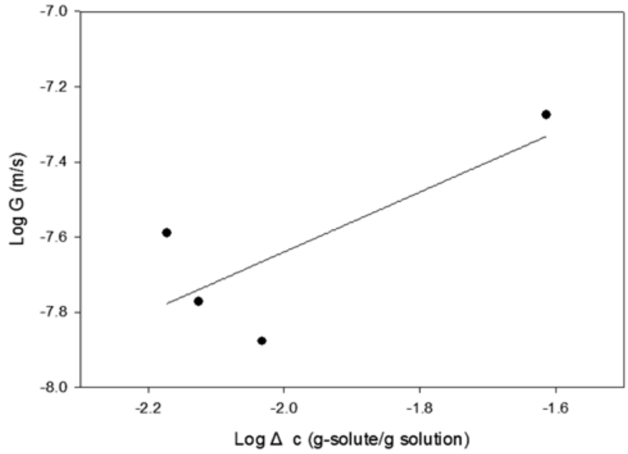


(a)

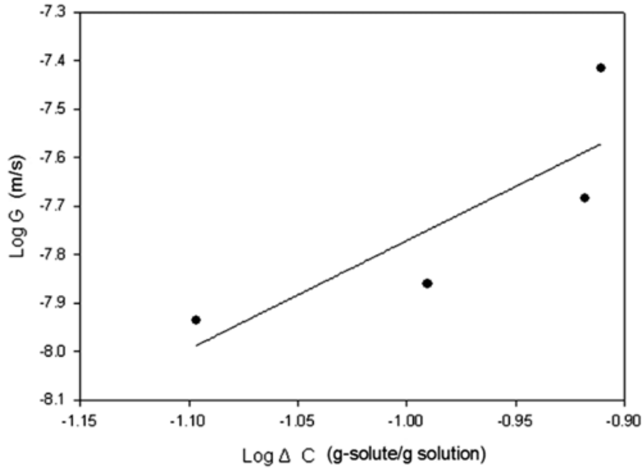


(b)

Fig. 5. Solubility in the KCl-water mixture (a) Reactive Black 8, (b) Reactive Blue 49.



(a)



(b)

Fig. 6. Log-Log plot growth rate versus concentration change (a) Reactive Black8, (b) Reactive Blue49.

Table 1. Growth rate constants obtained from logG vs. log ΔC plot (at 25 °C, 15 wt% KCl added)

Dye	k_g (m/s)	g	G
Reactive Black 8	0.964E-6	1.041	$0.964\times10^{-06}\ \Delta C^{1.041}$
Reactive Blue 49	2.922E-6	2.236	$2.922\times10^{-06}\ \Delta C^{2.236}$

the room temperature and its saturation solubility is independent of the temperature over approximately 25 °C, whereas the saturation solubility of RB49 increases slowly with increasing temperature, and it is less soluble than RB8. Fig. 5(a) shows the solubility of RB8 by KCl concentration at 25 °C, 30 °C and 35 °C, respectively. The solubility of RB8 was decreased by the higher temperature and concentration of KCl. Fig. 5(b) shows the solubility of RB49 by the KCl concentration at 25 °C, 30 °C and 35 °C, respectively. At low KCl concentration the solubility change was large; over the 10 wt% KCl concentration the solubility change was very little. RB49 was little soluble to RB8. Fig. 6 shows the growth rate plot of the RB8 and RB49. Growth rate constant, k_g, and order, g, were calculated from log-log plot of growth rate versus concentration change obtained by measuring concentration change and weight change during the experiment. The growth rates of RB8 and RB49 calculated empirically are very low (10^{-6} order), as shown in Table 1.

CONCLUSION

Dye crystal density and solubility and growth rate of dye were investigated. The density of RB8 crystal was 1.92 g/cm^3 and that of RB49 1.26 g/cm^3. The density of dye solution decreased linearly with the temperature. The saturation solubility to the water was constant over room temperature. The solubility of the dye solution decreased by the higher temperature and KCl concentration. The growth rate of RB8 was $0.964\times10^{-06}\ \Delta C^{1.041}$ and that of RB49 was $2.922\times10^{-06}\ \Delta C^{2.236}$, respectively.

NOMENCLATURE

A_T : total crystal surface area [m^2/kg solvent]
c : concentration [g solute/g solvent]
G : overall linear growth rate [m/s]
g : growth rate order
k_G : overall growth rate constant [m^{2}s(kg/kg)^g]
k_g : overall linear growth rate constant [s(kg/kg)^g]
L : crystal size
R : overall growth rate based on mass deposition [kg/m^{2}s]
t : time [s]
W : weight of crystals [kg]

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