

ON-LINE MEASUREMENT OF SUPERSATURATION DURING BATCH COOLING CRYSTALLIZATION OF AMMONIUM ALUM

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Introduction

Supersaturation, which is defined as the difference between actual and equilibrium concentrations of a solution, is a driving force in both nucleation and crystal growth processes. Its development during a batch operation affects considerably the final crystal size distribution. For obtaining crystals of a desired size distribution, it is useful to control the supersaturation.

Supersaturation is usually small as compared with the absolute concentration of a saturated solution. The concentration measurement technique must be sensitive enough to detect a small amount of deviation if it is applied for supersaturation measurement. It is also required to be quick enough when the supersaturation is used as a control variable. In this study an electrical conductivity method was tested. The system of ammonium aluminum sulfate-water was used as a model system.

Theory

Electrical conductivity is a function of solution concentration and temperature. If the concentration is expressed in terms of the saturation temperature t_N , at which temperature the solution is saturated, the conductivity V can be a function of t_N and the actual temperature t as follows.

$$V = f(t_N) + (t - t_N)g(t_N) \quad (1)$$

where the first term $f(t_N)$ gives the conductivity of a saturated solution and the second term the deviation due to the temperature difference $(t - t_N)$ from the saturation temperature. The coefficient $g(t_N)$ indicates the extent of the temperature effect.

If the temperature t and the conductivity V are measured for a given solution, the saturation temperature t_N , at which the solution would be saturated, can be calculated with Eq. (1). From t_N the

actual concentration is found by using the equation correlating solubility with temperature. Although many equations have been presented, that proposed by Broul *et al.*¹⁾ was used in this work.

$$\log x = A + B/(t + 273.16) + C \log(t + 273.16) \quad (2)$$

where x , expressed in mole fraction, is the solubility at the temperature t , and A , B and C are constants. The solubility, i.e., the equilibrium concentration, at the temperature t , is also given by Eq. (2). The difference between these two concentrations is the supersaturation.

Experimental

Conductivity measurement: Conductivity and temperature were measured for ammonium aluminum sulfate (ammonium alum) solutions in a crystallizer (see Fig. 1), which was also used for the next crystallization experiment. The crystallizer was a jacketed glass vessel (working volume: 10 l) fitted with a draft tube and a four-bladed propeller.

In a typical measurement, a solution was prepared from distilled water (conductivity: lower than $6 \mu\text{S}/\text{cm}$) and ammonium aluminum sulfate dodecahydrate crystals (extra-pure reagent). All the crystals were dissolved by agitation (1 h) at a temperature about 5°C higher than the saturation temperature. Then a sample solution of about 100 cm^3 was taken into an Erlenmeyer flask. The temperature at which all crystalline particles, once they appeared in the sample by cooling, disappeared on very slow heating, was measured and taken as the saturation temperature t_N ¹⁾.

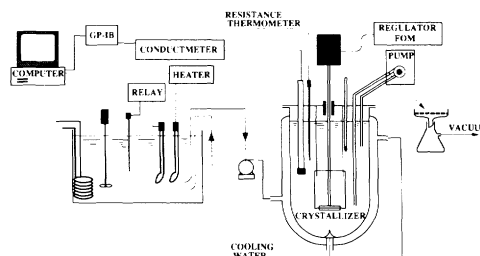


Fig. 1. Experimental apparatus

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Then the solution in the crystallizer was agitated and cooled at a rate of about 10, 25 or 50°C per hour until crystals appeared. During cooling the temperature was measured with a resistance thermometer (Resistance Bulb Class B, CHINO Co., Ltd. Japan). Conductivity was measured with an electrical conductmeter (Digital Conduct Meter CM-15A fitted with a cell CG 511 A, TOA Electronics Ltd. Japan). Temperature and conductivity were measured at intervals of 10 sec and all the data were collected in a computer (EPSON 386 S, SEIKO EPSON Corp. Japan) through a data logging meter (Digital Multilogging Meter AD 5312, A&D Co., Ltd. Japan). Conductivities were measured for solutions of 12 different concentrations to find the function $f(t_N)$ and the coefficient $g(t_N)$ in Eq. (1).

Crystallization experiment: A batch cooling crystallization experiment was performed to demonstrate how the supersaturation can be determined. The apparatus shown previously (Fig. 1) was used. At the beginning of the experiment the solution was saturated at 41.4°C. It was cooled to 25°C during a 4-h period. Change of temperature was controlled according to a policy of constant-rate supersaturation²⁾, in which policy the supersaturation would be created at a constant rate if no crystallization occurred. Conductivity and temperature were measured every 10 sec and the supersaturation was calculated by computer, using Eqs. (1) and (2). In calculation the Newton method was used for solving Eq. (1) for the saturation temperature t_N .

After the final temperature 25°C was reached, agitation of the solution was continued for an additional 2 h at the same temperature to make the solution saturated. The conductivity of the suspension thus obtained was recorded.

Results and Discussion

Figure 2 shows the conductivity of solutions of various concentrations, where the conductivity change with temperature is shown by short straight lines. The saturation temperature of each solution is marked by a circle. No effect of cooling rate was found. The conductivity of the saturated solution was fitted with the following equation as a function of t_N by using a least squares method.

$$f(t_N) = q_1 \exp(q_2 t_N) \quad (3)$$

and the coefficient $g(t_N)$, the slope of the short straight lines, was fitted with the following function. A least squares method was also used here.

$$g(t_N) = q_3 + q_4 t_N \quad (4)$$

The constants in Eqs. (3) and (4) thus determined were

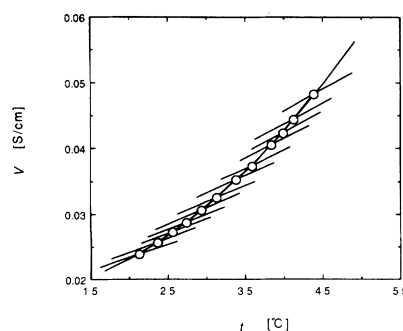


Fig. 2. Electrical conductivity vs. temperature for various concentrations of solutions

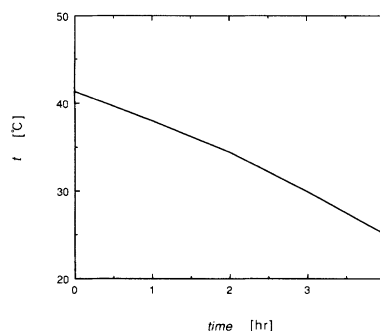


Fig. 3. Cooling curve

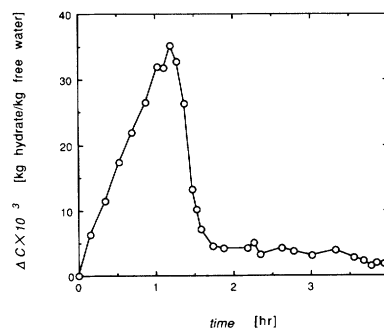


Fig. 4. Supersaturation measured vs. time

$$\begin{aligned} q_1 &= 0.0123 \\ q_2 &= 0.0311 \\ q_3 &= 1.54 \times 10^{-4} \\ q_4 &= 1.17 \times 10^{-5} \end{aligned} \quad (5)$$

The cooling curve is shown in **Fig. 3**, which is not linear. It was obtained, following the cooling policy mentioned above, by controlling the temperature with the computer. The corresponding supersaturation, expressed in the unit of kg hydrate/kg free water, is shown in **Fig. 4**. (In calculation of the concentration, the following values¹⁾ of the constants in Eq. (2) were used: $A = -80.6351$, $B = 2402.1635$, $C = 28.39789$.) At the early stage of the run, during which no crystals appeared, the supersaturation increased at a constant rate as expected from the cooling policy. About 40 min later a small amount of crystals appeared, but the

supersaturation still continued to increase linearly with time. After the highest supersaturation, 0.36 kg hydrate/kg free water, was attained at about 1 h, a cloud of crystals appeared within a few minutes and at the same time the supersaturation quickly dropped and once reached a value of about 0.005 kg hydrate/kg free water at 1.5 h. Then the supersaturation decreased gradually to 0.0015 kg hydrate/kg free water until the end of cooling. After the temperature change was halted at 25°C, the supersaturation dropped quickly to zero because of no creation of supersaturation. The conductivity of the suspension thus obtained did not change for two hours at this temperature, and it was the same as the conductivity of the saturated solution. No effect of the suspended crystals on the conductivity was found.

Equilibrium concentration was calculated to be 0.243 kg hydrate/kg free water at the beginning of the run and 0.132 kg hydrate/kg free water at the end. Accuracy of measurement of temperature was $\pm 0.1^\circ\text{C}$, which corresponds to a concentration of $\pm 1 \times 10^{-3}$ kg hydrate/kg free water and in the case of conductivity accuracy was $\pm 0.2\text{ mS/cm}$, which

corresponds to $\pm 1 \times 10^{-3}$ kg hydrate/kg free water. The conductivity changed from 44 mS/cm at the beginning to 26 mS/cm at the end of the run.

This method has possibilities as an advanced approach to on-line measurement of supersaturation that could be successfully applied to the control of a batch crystallization process.

Nomenclature

A, B, C	= constants in Eq. (2)
q_i	= constants in Eqs. (3), (4), (5) ($i=1, 2, 3, 4$)
Δc	= supersaturation, defined as the difference between an actual concentration and the solubility of the equilibrium concentration [kg hydrate/kg free water]
t	= temperature [$^\circ\text{C}$]
t_N	= saturation temperature [$^\circ\text{C}$]
V	= electrical conductivity [S/cm]
x	= concentration [mole fraction of hydrate]

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- 2) Mullin, J. W. and J. Nývlt: *Chem. Eng. Sci.*, **26**, 369 (1970).