Precise Determination of Supersaturation by Temperature Float Method

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Supersaturation is the driving force in the crystallization process. It is very difficult, however, to determine precisely the supersaturation and to correlate it with kinetic data of crystallization, because the relative supersaturation is very low, e.g., 0.01 or less, for many inorganic chemicals. As an alternative approach, population balance was proposed for the study of crystallization kinetics without supersaturation data (Randolph and Larson 1988). However, population balance is used as a technique for performance analysis rather than for design of industrial crystallizers. The scale-up and design of crystallizers have yet to depend on empirical methods, due to the lack of reliable supersaturation data (Bennett, 1984; Qian et al., 1987).

In this paper, a temperature float technique is proposed for determining the relative supersaturation of potassium chloride as precisely as 10^{-4}.

Method and Apparatus

Supersaturation of the solution in a crystallizer has been determined by many investigators using direct chemical analysis or indirect measurement of viscosity, conductivity, refractive index or density of the solution. The errors of supersaturation are 0.03–0.04, 0.03, and 0.01 kg solute/100 kg solution by pycnometer (Garside and Jancic, 1979), refractometer (Bourne and Hungerbuehler, 1980), and oscillator densimeter (Tavare and Garside, 1986), respectively. Accuracies of other methods are even poorer. Thus, previous methods are not precise enough for systems having narrow width of metastable zone, e.g., a KCl-H_2O system.

Although the temperature float method has been well established for the precise determination of deuterium content in water or heavy water (Shatenstein et al., 1957), it can be used only in a very narrow range of concentration and needs a reference solution as a standard. In this work we implant this method for precise determination of supersaturation using its corresponding saturated solution as the reference solution.

The general principle, apparatus, and procedure of temperature float method have been detailed by Shatenstein et al. (1957). Only the basic concept and main apparatus are outlined here.

A submerged float is in an equilibrium state with its surrounding solution in a tube, called float tube, when the solution density is matched to the float density by the adjustment of the solution temperature. This equilibrium temperature is called flotation temperature, T, and can be determined within +/− 0.001 K. Thus, it can be very precisely correlated for a given float density, d, with the corresponding solution concentration, C, or m. For this correlation, a density equation with eight parameters is proposed, to match the density data of many solutions in the ICT (Washburn, 1928) for the whole range of concentration at 273.15–313.15 K, by optimization on computer. The density equation of KCl solution is as follows:

$$\begin{aligned} d = {} & [0.99987 + 4.98147 \times 10^{-2}\mathrm{m} - 2.90902 \times 10^{-3}\mathrm{m}^2 \\ & + 1.83243 \times 10^{-2}(T - 273.15) - 1.03671 \\ & \times 10^{-5}(T - 273.15)^2 + 1.4631 \times 10^{-4}\mathrm{m}^3 + 7.1878 \\ & \times 10^{-4}\mathrm{m}(T - 273.15) - 2.0194 \times 10^{-5}\mathrm{m}^2 \\ & \times (T - 273.15)]/[1 + 1.82274 \times 10^{-2}(T - 273.15)] \end{aligned} \tag{1}$$

The density equation of NaCl solution is:

$$\begin{aligned} d = {} & [0.99987 + 4.41338 \times 10^{-2}\mathrm{m} - 2.11161 \times 10^{-3}\mathrm{m}^2 \\ & + 1.79726 \times 10^{-2}(T - 273.15) - 1.06178 \\ & \times 10^{-5}(T - 273.15)^2 + 0.84689 \times 10^{-4}\mathrm{m}^3 + 5.88258 \\ & \times 10^{-4}\mathrm{m}(T - 273.15) - 1.1320 \times 10^{-5} \\ & \times \mathrm{m}^2(T - 273.15)]/ \\ & [1 + 1.78710 \times 10^{-2}(T - 273.15)] \end{aligned} \tag{2}$$

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Their standard deviations, σ_n, are 8.0×10^{-5} and 6.5×10^{-5} g/cm^3 for KCl and NaCl solutions, respectively.

The spindle shape float, called superior by Tschang (1960), is *used in this work*. A special float tube having an inner stopper with an attached capillary (Huang and Zhang, 1983) has proven very suitable for this technique. The details of our float, float tube, and procedure are given in the Supplementary Material, available upon request. Also contained there are the equation derivations of $(\partial d/\partial m)_T$, $(\partial d/\partial T)_m$, and $(\partial T/\partial m)_d$, as well as density equations for KNO_3, KBr, NaBr, $LiNO_3$, KI, NaI, RbCl, RbBr, and CsBr solutions. Calculation shows that our method can also be applied to these or other systems, in which the density is sensitively dependent on both concentration and temperature of the solutions.

Experimental Results

Concentration and flotation temperature for unsaturated solutions

These tests give the accuracy of this method itself, excluding the sampling error. All solutions are prepared with analytical reagents and distilled water.

Dilute Solution. A suitable float is selected for determining flotation temperatures, *T*, of 20 solutions in the concentration, *C*, range of 1.069–1.327 g KCl/100 g H_2O. A linear relationship between *T* and *C* is well correlated, as illustrated by Figure 1 and by the following equation:

$$T = 17.148\,C + 291.241 \qquad (3)$$

with a correlation coefficient 0.9997, and standard deviation σ_{n-1} 1.92×10^{-3} g KCl/100 g H_2O, this method's supersaturation precision.

Substituting the arithmetical average of flotation temperature, $\overline{T}$, of 311.450 K, and that of concentration, $\overline{C}$, of 1.1785 g KCl/100 g H_2O, i.e., $\overline{m}$ of 0.1581 gmol · KCl/kg H_2O, into the equation of $(\partial T/\partial C)_d$, we have

$$(\partial T/\partial C)_d = 17.335\ \mathrm{K/(g\ KCl/100\ g\ H_2O)}$$

This value agrees well with the regression line slope in Figure 1, i.e., 17.148 K/(g KCl/100 g H_2O). The relative deviation is only 1.08%.

Concentrated Solution. Another float is used for 17 solutions in the concentration, *C*, range of 19.373–19.497 g KCl/100 g H_2O. The density of the float is calibrated with six standard NaCl solutions, using Equation 2. The calculated densities agree with one another within $+/- 5 \times 10^{-6}$ g/cm^3. For these KCl solutions, the linear relationship between *T* and *C* is well correlated by Eq. 4 and shown in Figure 2.

$$T = 11.348\,C + 83.659 \qquad (4)$$

The correlation coefficient of Eq. 4 is 0.9977. The standard deviation, σ_{n-1}, is 2.7×10^{-3} g KCl/100 g H_2O, or 2.3×10^{-3} kg KCl/100 kg solution, the accuracy of the method itself. There is a systematical error of 1.46×10^{-2} g KCl/100 g H_2O between the concentrations calculated by Eqs. 1 and 2, and those directly obtained from weights of potassium chloride and distilled water. This is attributed mainly to the errors in Eqs. 1 and 2, as well as to the impurity of NaCl in the AR potassium chloride. However,

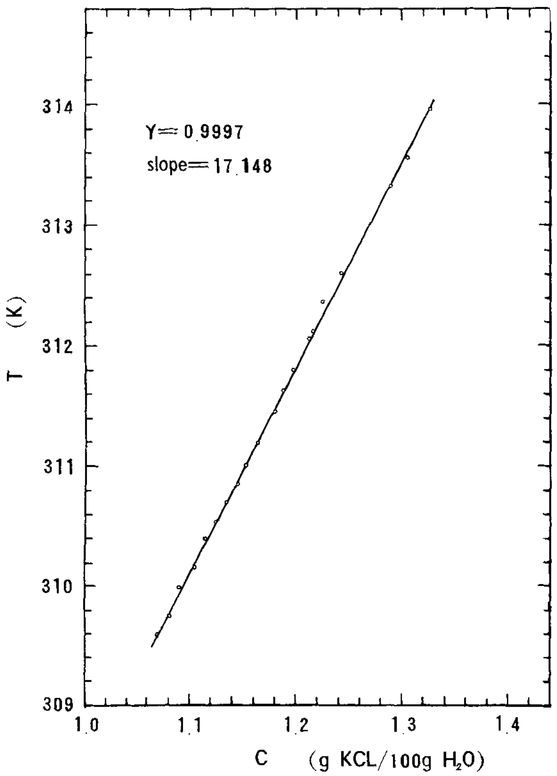

Figure 1. Flotation temperature vs. potassium chloride concentration for dilute solution.

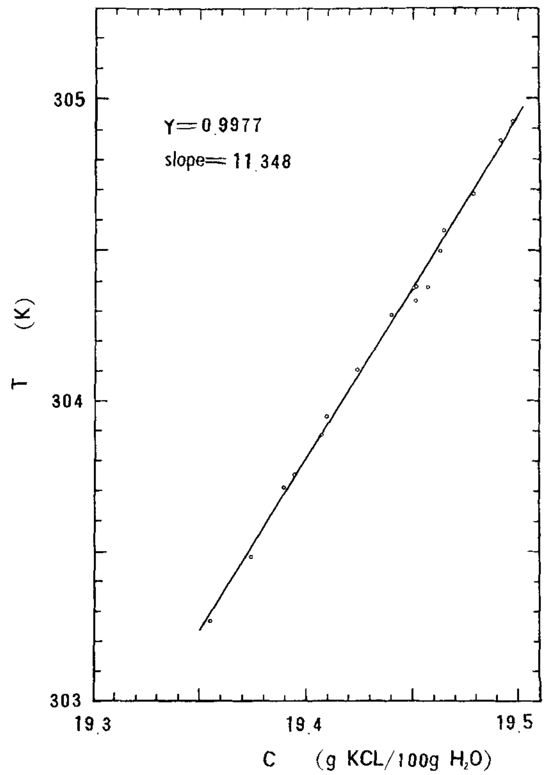

Figure 2. Flotation temperature vs. potassium chloride concentration for concentrated solution.

this systematical error is offset in the supersaturation determination.

Substituting the arithmetical average of flotation temperature, $\overline{T}$, and concentrtation $\overline{C}$, with 304.203 K and 19.435 g KCl/100 g H_2O, respectively, in $(\partial T/\partial C)_d$ equation, we have

$$(\partial T/\partial C)_d = 11.403 \text{ K/(g KCl/100 g H}_2\text{O)}$$

The value agrees very well with the slope of regression line in Figure 2, of 11.348 K/(g KCl/100 g H_2O). The relative deviation is only 0.48%.

Thus, the deviation of $(\partial T/\partial C)_d$ for both dilute and concentrated solutions can be neglected in supersaturation determination.

Solubility and saturation temperature

This test for saturated solution gives the accuracy of supersaturation including errors of sampling and preparation of saturated solution.

A third float is calibrated with another set of six standard sodium chloride solutions. Saturated KCl solution is prepared with recrystallized large crystals from AR potassium chloride, and distilled water. The saturation temperature is controlled within ± 0.001 K under a gentle stirring of the solution. After the saturated solution is completely settled, a 5 cm^3 sample is taken with a slightly preheated pipet. Twenty-six experiments are made in the saturation temperature, T_s, range of 298.13–303.15 K. The solubility, C_s, is calculated from the flotation temperature, T, and the density, d. The regression line of C_s versus T_s is shown in Figure 3, and is expressed as follows:

$$C_s = 0.29180\ T_s - 51.105 \qquad (5)$$

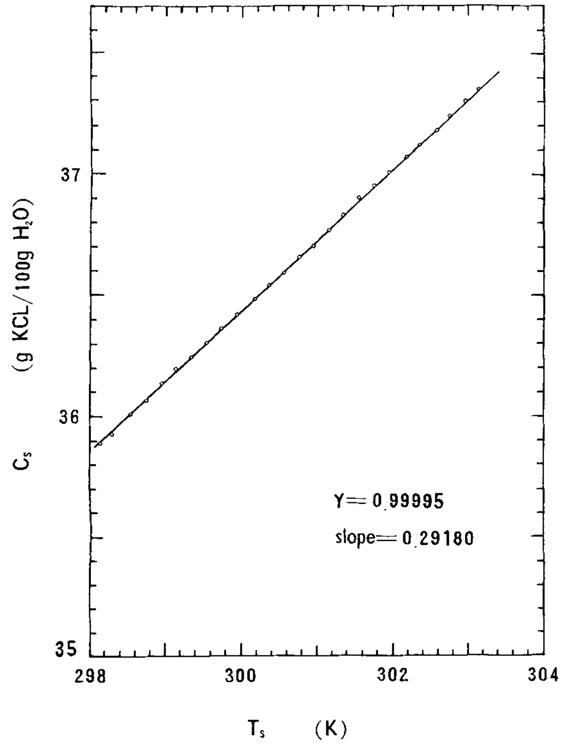

Figure 3. Concentration of saturated potassium chloride solution vs. saturation temperature.

The correlation coefficient is 0.99995. The standard deviation, σ_{n-1}, of 4.3×10^{-3} g KCl/ 100 g H_2O, or 3.0×10^{-3} kg KCl/100 kg solution, is only 0.011% of the solubility. This accuracy includes the errors introduced by the sampling procedure and preparation of saturated solution.

When we use this method to determine supersaturation, we just compare the flotation temperature of supersaturated solution with that of corresponding saturated solution. From the temperature difference, ΔT, supersaturation, ΔC, can be calculated by the following equation:

$$\Delta C = (\partial C/\partial T)_d\, \Delta T \qquad (6)$$

For the T_s range of 301.97–303.15 K in the last seven experiments, the value of $(\partial T/\partial C)_d$, from the slope of regression line, C_s versus T, is 0.12155 g KCl/100 g H_2O. This value, directly from the $(\partial T/\partial C)_d$ equation, is 0.12134 g KCl/100 g H_2O, with the arithmetical average values of $\overline{C}_s$ for 37.183 g KCl/100 g H_2O, and $\overline{T}$ for 310.426 K.

For the supersaturation determination in a KCl crystallizer at a crystallization temperature of 303.1–303.2 K, the following equation is precise enough:

$$\Delta C = 0.122\, \Delta T \qquad (7)$$

Similarly, for other systems which offer reliable density equations for the calculation of $(\partial C/\partial T)_d$, only the difference of flotation temperature, ΔT, needs to be carefully measured.

We have determined the supersaturation of KCl solution in a continuous MSMPR crystallizer at 303.11 K, by this method. The experimental error of ΔC is 0.004 g KCl/100 g H_2O, only 4% of ΔC and 0.01% of the solubility, C_s.

In summary, this paper has proposed a much better method for supersaturation determination, with an accuracy of 0.003 kg/100 kg solution. It is useful for those systems in which the solution density is sensitively dependent on both concentration and temperature.

Notation

C = concentration of solution, g KCl/100 g H_2O
C_s = solubility, g KCl/100 g H_2O
ΔC = supersaturation, g KCl/100 g H_2O
d = density of solution, g/cm^3
m = concentration of solution, gmol · KCl/100 g H_2O
T = temperature or flotation temperature, K
T_s = saturation temperature, K
ΔT = flotation temperature difference between supersaturated and saturated solutions, K

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