Precipitation of Sodium Acetate Trihydrate
from Its Supersaturated Solution

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The rate of crystallization of sodium acetate trihydrate from a super-saturated solution in water was measured by seeding the solution contained in a 50-cm long tube at one end, and measuring the speed at which the solid-liquid boundary advanced. The rate of crystallization was found to increase directly with the concentration of the solution, in accordance with the equation proposed by Wilson and Frenkel. The rate was found to be independent of the temperature in the range of the concentrations studied. This has been explained in terms of a cancellation of opposite effects: that of the degree of supersaturation on the one hand and of the viscosity and diffusion on the other.

INTRODUCTION

Both the theoretical and the experimental aspects of the kinetics of crystal growth have been studied extensively[1-6]. Much of the work has concentrated on the phenomenon, and the growth of single crystals. On the other hand, the kinetics of seed-initiated precipitation from highly supersaturated solutions has received scant attention[7,8]. We report the kinetics of precipitation of sodium acetate trihydrate from its supersaturated solution, initiated by seeding. The system is ideally suited to studies of the rate of precipitation, since the supersaturated solution is kinetically stable, and in the absence of seeding, will stay as solution almost indefinitely. It is possible to study a fair range of concentrations at several different temperatures.

EXPERIMENTAL

The solutions were made by adding the required mass of the salt and water in an Erlenmeyer flask and heating over a hot plate with stirring till the mixture became a homogeneous liquid. While still hot, the solution was carefully added to a graduated tube of 1 cm diameter. The tube was shaped from a laboratory burette by cutting the lower end and sealing it off. The solution was allowed to cool down to the temperature of the experiment. The values of the equilibrium concentrations, C_{EQ}, of the salt were taken from literature[10]. These are 36.3, 46.4 and 65.5 g of the salt per 100 g of water at 0, 20 and 40°C respectively. The values at other temperatures were obtained from interpolation.

For the measurement of the rate of precipitation, the tube was suspended vertically in a large (500 mL) cylinder, which was filled with water at the temperature of the experiment. After thermal equilibrium was reached, the exact temperature of the water in the cylinder was measured. To start the precipitation,

a particle of solid sodium acetate, the size of a grain of sand, was dropped onto
the surface of the supersaturated solution, and the stopwatch was started. The
process of crystallization started immediately, and a well-defined front of the
crystallized salt started moving down. The time at which the boundary moved
past the graduations (usually 2 cm apart) was noted, until the crystal boundary
reached the other end of the tube. The water in the cylinder was stirred conti-
nuously during the measurement. The temperature of the water was measured
after the precipitation was complete. For measurements at 0°C, ice-water mixture
used in the cylinder and for temperature below 0°C, an appropriate mixture of
ice, water and NaCl was used.

RESULTS AND DISCUSSION

The rate of crystallization of sodium acetate trihydrate, as measured by the
speed of the movement of the solid-solution boundary in a supersaturated solution
contained in a glass tube, was constant with time throughout the process. This is
shown in Fig. 1, where the plot of the position of the boundary against time is a
straight line. For these high concentrations studied, the advancing boundary is
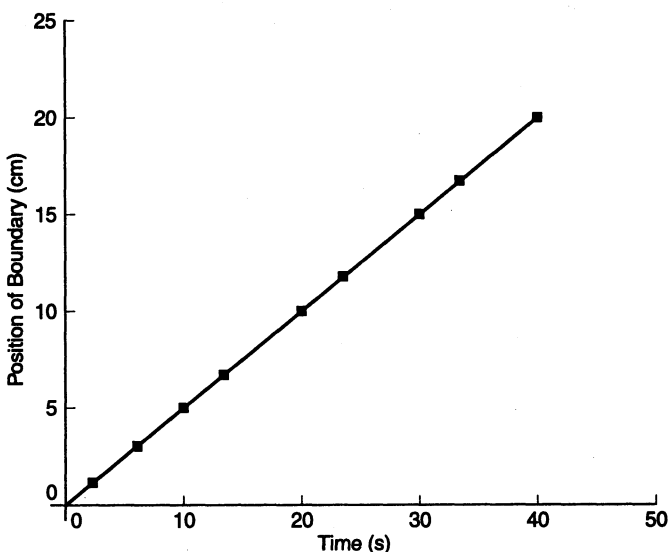horizontal, sharp and well defined, allowing precise measurements of the rate.

Fig. 1.   The position of the advancing solid-solution boundary as a function of time at 0°C . The
solution concentration was 5 g sodium acetate trihydrate per g water.

This uniformity of the rate can be understood by considering the conditions
prevailing just adjacent to the boundary at any time during the process. Before
the start of the process, the composition and the temperature of the solution are
uniform throughout the tube. The conditions just ahead of the moving boundary
remain the same no matter where the boundary is at any particular time. These
conditions include any that may affect the rate of crystallization, *i.e.*, temperature,
composition and viscosity. High values of viscosity, which prevail at these

concentrations, ensure that the crystallization taking place in one region does not affect the value of the concentration in another region. Since identical conditions prevail in all regions, they cause identical rates of advancement of the boundary.

Effect of Concentration: The rate of crystallization was found to increase linearly with the relative supersaturation. $\sigma = (C - C_{EQ})/C_{EQ}$, (Fig. 2). C is the concentration (in mass of the salt dissolved per unit mass of water), and C_{EQ} is the equilibrium saturated concentration of the salt at the particular temperature. The system is thus seen to follow the Wilson-Frenkel maximum growth law[9]. This is expected under the conditions of the experiment. The derivation of the Wilson-Frenkel law assumes that the rate of dissolution of the crystal is not affected by the changes in the solution phase. In this experiment, the advancing solid continuously encounters fresh solution and the conditions faced by the boundary are exactly the same at all stages of the process. Thus, for the process, we can write:

$$R = \beta(C - C_{EQ})/C_{EQ.}$$

Here R is the rate of growth of crystals and β is a constant.
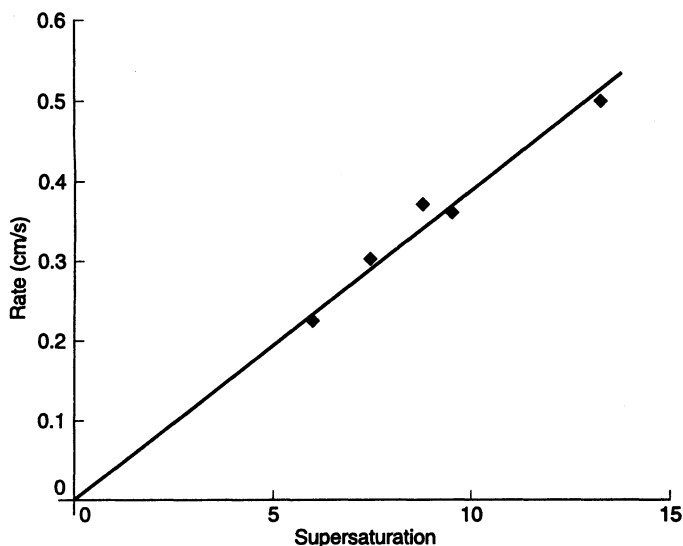

Fig. 2.   Rate of advancement of the boundary as a function of relative supersaturation at 0°C.

Effect of Temperature: A variation in temperature can affect the rate of crystallization through its effect on the degree of supersaturation, viscosity and the diffusion coefficient of the solution. As the temperature of a solution is increased, its supersaturation $(C - C_{EQ})/CC_{EQ}$ decreases, since C_{EQ} increases with temperature. The viscosity of a solution also decreases, while the diffusion coefficient increases with increasing temperature. At higher temperature, therefore, on the one hand, the rate of crystallization decreases because of the decreased supersaturation, but on the other hand the rate increases because of the changes in viscosity and the diffusion coefficient.

The results, shown in Fig. 3, indicate that these opposite effects roughly cancel out in this system in the temperature ranges of –10°C to 35°C for a solution whose concentration is 5.0 g/g-water.
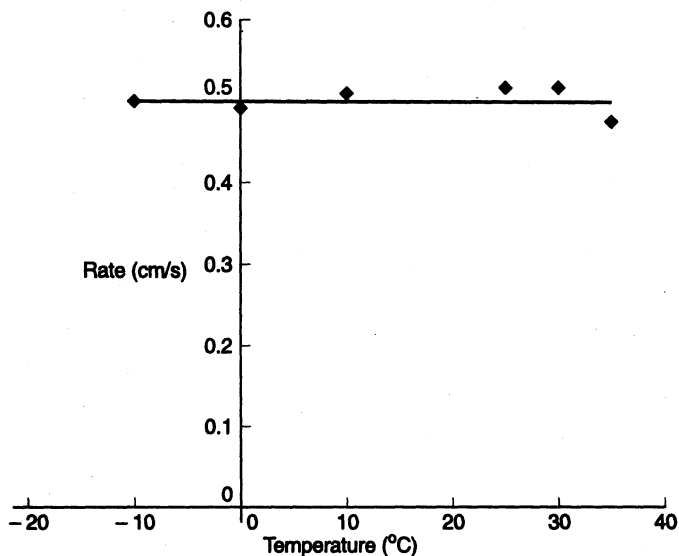

Fig. 3.   The rate of advancement of the boundary as a function of temperature. The solution concentration was 5.0 g sodium acetate trihydrate per g water.

Conclusion

The rate of crystallization from a supersaturated solution of sodium acetate trihydrate increases linearly with supersaturation, but is not affected significantly by a change of temperature. The concentration-dependence is in accordance with the Wilson-Frenkel equation. The non-dependence of the rate of crystallization on temperature is explained in terms of a cancellation of the effects of supersaturation, viscosity and diffusion.

<div align="center">REFERENCES</div>

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