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The Fractionation of Tritium in the Crystallization of Inorganic Hydrates from a Tritiated Solution

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Bennema's theory of crystal growth from a solution was modified and used in explaining fractionations of tritiated water in the crystal-growth processes of several inorganic hydrated salts from concentrated aqueous solutions. It was suggested that some water molecules in the aqueous solutions were free to become growth units which are not necessarily activated for entering the crystal surface. The dilution of tritiated water in the crystal was observed; this was explained in a satisfactory way in terms of the surface-diffusion model originally proposed by Burton, Cabrera, and Frank. On the contrary, the volume diffusion model was inadequate for interpreting the fractionation of tritium.

The theory of crystal growth from the vapor phase has been extensively developed, and there is sufficient experimental evidence supporting the concept of surface diffusion which regulates the growth mechanism.[1] The crystal growth from a solution, however, has been scarcely at all treated from the theoretical point of view. The kinetics of crystallization from a solution becomes more complicated because of the interaction and solvation of constituent ions, although there is no essential difference between the growth from vapor and that from a solution.

The rate of crystal growth from a solution is assumed to depend on the advance velocity of the steps. It is, in turn, a problem whether or not a surface diffusion of growth units plays an essential role in the growth process. This point has been discussed on the basis of the morphological theory of Hartman and Perdok, and the surface diffusion has been found to be an essential process in the crystal growth.[2] Recently Bennema[2,3] has explained his accurate data on the crystal growth by assuming the surface-diffusion model of Burton, Cabrera, and Frank.[1]

On the basis of these works it has come to seem probable that crystal growth from solution at a low supersaturation also occurs with the surface-diffusion process. However, there has thus far been little discussion of the mechanism of the crystal growth of inorganic hydrates, especially those from concentrated aqueous solutions. This is probably due to the complicated behavior of growth units in solutions. The aim of the present paper is to discuss the mechanism of the crystal growth of several inorganic hydrated salts from aqueous solutions in the light of the fractionation of tritiated water.

There have been a few papers studying the fractionations of heavy water (but not that of tritiated water) in the growth processes.[4,5] These results have been discussed from the points of view of the vapor pressures of the ctystal and the solution or from that of the hydrogen bonding of water, but not on the basis of the theory of crystal growth from a solution. On the contrary, it may be possible, under the present experimental conditions, to use the crystal-growth theory from a solution, which is useful at low supersaturations up to *ca.* 20%, in explaining the fractionations of tritiated water. A trace amount of tritiated water was present in a solution of inorganic salt; its fractionation was examined when the salts were crystallized with water of hydration and much attention was paid to the behavior of water crystallized from the solution.

Experimental

Large single crystals of sulfates of cobalt, nickel, and copper were grown from unstirred solutions by evaporating the solvent containing a trace amount of tritiated water (*ca.* 1.0×10^{-6} mol/ml). A single crystal of cobalt sulfate was obtained at 30.0°C, while others

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1) W. K. Burton, N. Cabrera and F. C. Frank, *Phil. Trans. Roy. Soc.*, **243**, 299 (1951).

2) P. Bennema, Thesis, The Technical University of Delft (1965).

3) P. Bennema, *J. Cryst. Growth*, **5**, 29 (1969).

4) R. M. Barrer and A. F. Denny, *J. Chem. Soc.*, **1964**, 4677.

5) M. Johansson and K. E. Holmberg, *Acta Chem. Scand.*, **23**, 765 (1969).

were obtained at 40.0°C. The rates of crystal growth were so slow that only 3 or 4 g of the crystals were obtained in two weeks. The water of hydration was recovered by heating the single crystal until no further dehydration was observed.

The tritium contents in the dehydrated water were compared with those of the mother liquid by observing their activities. The activity measurements were done by a liquid scintillation counter, a Packard Model 2002 Tri-Carb Scintillation Spectrometer. As the scintillant we used a solution composed of toluene, ethylene glycol monomethyl ether, 2,5-diphenyloxazole (PPO), and 1,4-bis-2′-(5′-phenyloxazolyl)benzene (POPOP).

Results and Discussion

The observed fractionations of tritiated water are summarized in Table 1; the table shows that all the separation factors are less than unity, implying the dilution of tritiated water in the hydrate crystal. The separation factor, S, for the equilibrium between solid and liquid phases is usually defined by:

$$S = \{N_s/(1-N_s)\}\{(1-N_l)/N_l\}, \quad (1)$$

where N_s and N_l are the mole fractions of a given isotope (tritiated water, in the present case) in the solid and liquid phases respectively. Since N_s and N_l are extremely small in the present study, Eq. (1) can be simplified to:

$$S = N_s/N_l. \quad (2)$$

Table 1. Separation factor of tritiated water, S, observed in the crystallization of the sulfate from its solution

Crystal	$S_{obs.}$
$CoSO_4 \cdot 7H_2O$	0.979 ± 0.007
$NiSO_4 \cdot 7H_2O$	0.972 ± 0.011[6]
$CuSO_4 \cdot 5H_2O$	0.956 ± 0.012[7]

Theories of Crystal Growth from a Solution. Recently, Bennema has applied the spiral crystal growth model of Burton *et al.*, derived from the vapor phase, to that from a solution.[3] According to his treatment, the rate of crystal growth, R, from a solution at a low supersaturation is given as follows:

$$R = \beta c_0 \Omega (kT/h) A N_0 \exp(-H/kT)(\sigma^2/\sigma_1)\tanh(\sigma_1/\sigma), \quad (3)$$

where the notations are as given below:

β=retarding factor arising if the relaxation time for a growth unit's entry into a kink is small
c_0=retarding factor arising if $x_s \ll x_0$
x_s=mean displacement of a growth unit on the surface
x_0=mean distance between the kinks
Ω=volume of a growth unit in the crystal
k=Boltzmann's constant
T=absolute temperature
h=Planck's constant
A=thickness of the adsorption layer
N_0=equilibrium concentration of growth units per cm³ in the solution
H=dehydration activation energy for an entry of growth units into the adsorption layer
σ=relative supersaturation
$\sigma_1 = 9.5\ \gamma a/(\varepsilon k T x_s)$
γ=edge free energy of a step of the length of a
a=the shortest distance between growth units
ε=measure of the number of interacting spirals

Equation (3) may be useful in estimating the rate of integration of an ion into the crystal in the case of the growth of an ionic crystal from the aqueous solution.

A modified equation has to be used for estimating the rate of integration of water in the growth of hydrated ionic crystals from aqueous solutions, assuming for the moment that some water molecules integrate independently of ions. For this purpose, the spiral crystal-growth theory from vapor by Burton *et al.*[1] may properly be used. According to this theory, the following relation holds between R and σ, assuming that the diffusion of growth units on the surface determines the growth rate:

$$R = C(\sigma^2/\sigma_1)\tanh(\sigma_1/\sigma). \quad (4)$$

The constant, C, will be given below for a free water molecule integrating from the solution to the crystal surface.

Assuming, further, that the integration occurs without activation, we can use a model for the mobile adsorption layer[8] much like that used for the growth theory from vapor discussed by Bennema.[2] The n_{s0}/N_0 ratio is thus given as follows for the equilibrium between the water molecules (growth units in this case) in the solution and those on the surface:

$$n_{s0}/N_0 = \{h/(2\pi m k T)^{1/2}\}\exp(A/kT), \quad (5)$$

where n_{s0} is the equilibrium concentration of growth units per cm² on the surface, m is the mass of a growth unit, and A is the energy difference between growth units in the solution and those on the surface. We should note here that one translational degree of freedom is lost if a growth unit is adsorbed onto the surface from the bulk solution. In Eq. (5) we disregard the fractions of reflected molecules striking the surface and the changes in the degrees of freedom other than the translational.

Accordingly, it follows from Eq. (5) and some lengthy treatments[1,2] that:

$$C = \alpha\beta c_0 \Omega N_0 k T/(2\pi m k T)^{1/2}. \quad (6)$$

The α factor is introduced as a correction for the growth from a solution, which is assumed to be

6) H. Tanaka and H. Negita, *J. Sci. Hiroshima Univ., Ser. A-II*, **32**, 299 (1968).
7) H. Tanaka, K. Hiraga and H. Negita, *J. Sci. Hiroshima Univ., Ser. A-II*, **33**, 243 (1969).
8) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York (1941), P. 350.

independent of the hydrogen isotopes. If the surface diffusion of a growth unit is an essential process in the growth process, Eq. (6) is simplified and combined with Eq. (4) to give rise to:

$$R = \alpha c_0 \Omega N_0 (kT/2\pi m)^{1/2} (\sigma^2/\sigma_1) \tanh(\sigma_1/\sigma), \quad (7)$$

since the value of β becomes unity. On the other hand, if the volume-diffusion model for the growth from a solution is adopted, in which model a growth unit is directly transported from the solution to the kink without any surface diffusion, the rate of the crystal growth is given by:

$$R = \{2\pi\lambda\varepsilon\beta D N_0 \Omega kT/(19\gamma a x_0)\}\sigma^2, \quad (8)$$

where λ is the mean distance between one equilibrium position and a neighboring one in the solution, and where D is the volume-diffusion constant. The volume-diffusion model was discussed extensively by Bennema on the basis of the original theory of Burton *et al.*[2] We may note here that both Eqs. (7) and (8) are adequate in considering the crystal growth from a well-stirred solution at a low supersaturation.

Water and Ions in a Concentrated Solution. In concentrated aqueous solutions of inorganic salts, a given ion can not exist independently of other ions and water molecules; *i. e.*, the system is very complicated due to complex formation and the hydration of ions. The complexes can be divided into two types, outer-sphere and inner-sphere complexes.[9] The process of inner-sphere-complex formation in the sulfates of divalent cations may be formulated as follows, with the successive release of intervening water molecules:

$$M(OH_2)_p^{2+} + SO_4^{2-} \rightleftharpoons M(OH_2)_p^{2+}, SO_4^{2-} \rightleftharpoons M(OH_2)_{p-q}^{2+}, SO_4^{2-} + qH_2O,$$

where p is the hydration number of the M^{2+} ion in the dilute aqueous solution and where q is the number of water molecules dehydrated in the inner-sphere-complex formation ($0 \leqq q \leqq p$). In the scheme, the hydration of the anion and any quantum mechanical interaction of the anion with the cation are ignored.

The value of q can be larger than unity; that is, the remaining water molecules in the inner-sphere complex are subject to further dehydration. This point has been discussed by many workers on the assumption that complex formation occurs fundamentally because of coulombic forces between the oppositely-charged ions.[10] Further dehydration seems to be very probable, particularly in the case of the weak hydration of cations, as is the case with the present study. We can thus assume in the succeeding argument that extra water molecules are released from the hydration sheath of cations in the complex under the present conditions.

Estimation of Separation Factors. Recognizing that molecules of the same chemical species but labeled with different isotopes have the same structure and electronic configuration, we can obtain the ratios of R_{HTO}/R_{H_2O} for two cases.

(a) In the case of the surface diffusion, the following relation is derived from Eq. (7):

$$R_{HTO}/R_{H_2O} = (m_{H_2O}/m_{HTO})^{1/2} = 0.949, \quad (9)$$

where R_{HTO}/R_{H_2O} is the ratio of the integration of HTO to that of H_2O molecules into the crystal and where m_{H_2O}/m_{HTO} is the mass ratio of H_2O to HTO molecules.

(b) In the case of the volume diffusion;

$$R_{HTO}/R_{H_2O} = D_{HTO}/D_{H_2O} = 1, \quad (10)$$

where D_{HTO}/D_{H_2O} is the ratio of the diffusion constants of HTO to H_2O molecules in the solution.

Equations (9) and (10) are supported by the following considerations:

(1) σ_1, which is a function of the mean displacement of a growth unit, X_s, may be independent of the mass of water, supposing that growth units in the activated state and those in the non-activated state on the surface have the same degrees of freedom.

(2) The retarding factor, β, in Eq. (8) is a function of relative supersaturations around the steps and the kinks, and the factor, c_0, is a function of both the mean distance between the kinks and the distance between successive turns of the spiral. Therefore, the values of β and c_0 should be unchangeable in a system with a trace amount of tritiated water, though these factors play an important role in determining the mechanism and the absolute value of R in the growth process.

(3) The value of D may be practically independent of the hydrogen isotope of the water molecule, as seen from the work by Wang *et al.*[11]

(4) The other factors in Eqs. (7) and (8) may also be unaffected by the presence of tritiated water.

Accordingly, we can estimate the separation factors from either Eq. (9) or (10), assuming that fractionations of tritiated water occur, if at all, only with free water molecules and not with the hydration water of cations. When hydrated cations

Table 2. Possible growth units and separation factor, S, calculated by Eq. (9)

Crystal	Growth units assumed	$S_{cal.}$
$CoSO_4 \cdot 7H_2O$	$Co(OH_2)_3^{2+}$, SO_4^{2-} and $4H_2O$	0.791
$NiSO_4 \cdot 7H_2O$	$Ni(OH_2)_3^{2+}$, SO_4^{2-} and $4H_2O$	0.971
$CuSO_4 \cdot 5H_2O$	$Cu(OH_2)_2^{2+}$, SO_4^{2-} and $3H_2O$	0.969

9) F. Basalo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York (1967), p. 34.

10) For example; J. E. Prue, *J. Chem. Educ.*, **46**, 12 (1969).

11) J. H. Wang, C. V. Robinson and I. S. Edelman, *J. Amer. Chem. Soc.*, **75**, 466 (1953).

are assumed to be "half-undressed" in the concentrated solutions, the values of S may be given as follows from Eq. (9):
(a) For $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$ $S = (3 \times 1.000 + 4 \times 0.949)/7 = 0.971$, (b) for $CuSO_4 \cdot 5H_2O$ $S = (2 \times 1.000 + 3 \times 0.949)/5 = 0.969$. Table 2 shows the species of growth units assumed, and the corresponding values of S estimated, as above.

From Eq. (10), which is based on the volume-diffusion mechanism, on the other hand, the values of S become unity, irrespective of the number of free water molecules as well as of the species of the growth units.

Factors Affecting the Separation Factor. There are various factors which affect the separation factor. Among them, those cited below may be most important:

(1) Inner-sphere complexes may be easily formed with an increase in the concentration of the solution, giving rise to more free water molecules and, thus, to a larger fractionation of tritiated water.

(2) The dehydration of ions in a solution should tend to occur at higher temperatures, thus leading to an increase in the fractionation of tritiated water.

(3) The weaker hydration of the cation may favor the release of the molecules from the inner-sphere complex,[12] which will in turn make the fractionation larger.

(4) Rapid crystallization (growth from a highly-supersaturated solution) may result in less fractionation of tritiated water, since it can be assumed that the equilibrium is no longer attained between growth units in the solution and the crystal surface.

(5) The situation becomes complicated at a high concentration of the hydronium ion because of proton transfer through water and proton injection into the crystal.[13] The effect on the fractionation of tritium can be neglected when the concentration of H_2TO^+ is very low.

Fractionation of Tritium and Crystal Growth. (1) Since the agreement between the calculated values of S listed in Table 2 and the experimental values seems to be satisfactory, it may be noted qualitatively that some dilution of tritiated water occurs in the hydrated salts. This ambiguity, however, may be inevitable at this stage, because many assumptions are involved in the preceding argument, especially because the number of free water molecules is adjustable.

(2) The point in our argument is not the absolute value of crystal growth rate, R, but the ratio of R_{HTO}/R_{H_2O}. Although the crystal growth process from an unstirred solution is influenced by the mass-transfer of a growth unit, the ratio of R_{HTO}/R_{H_2O} may be unaffected by the mass-transfer, since the D_{HTO}/D_{H_2O} ratio is nearly equal to unity.

(3) Free water molecules, in fact, can not integrate into the crystal independently, but crystallize accompanying the ion with the lowest relaxation time, since growth units are fixed into the crystal in a stoichiometric way. We presume, however, that it should be possible to obtain the ratio of R_{HTO} to R_{H_2O} either from Eq. (7) or from (8).

(4) Even if the spiral-growth model employed above might be partly disturbed by two-dimensional nuclei formed between steps at a higher supersaturation,[14] it is probable that the surface-diffusion mechanism is not seriously affected by the possible disturbance. We can thus estimate the ratio of R_{HTO} to R_{H_2O} independently of the nucleation, since the growth of the nuclei results from the surface diffusion and the subsequent integration of growth units into the kinks.

(5) It may be generally accepted that water molecules of crystallization come partly from free water in a solution and partly from hydration water in the growth of a hydrated crystal, recognizing that, practically, the latter is not subject to the fractionation of tritiated water.

(6) From the fact that the concept of the surface diffusion for crystal growth from a solution is adequate to explain the experimental results, while the concept of volume diffusion is not, it may be concluded that: (a) some free water must enter the crystal by the surface-diffusion mechanism and (b) inogranic hydrated sulfates probably crystallize, also *via* a process of the surface diffusion of growth units.

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12) D. R. Rosseinsky, *J. Chem. Soc.*, **1962**, 785.
13) D. F. Williams, B. Sykes and W. G. Schneider, *Can. J. Chem.*, **45**, 1109 (1967).
14) P. Bennema, R. Kern and B. Simon, *Phys. Status Solidi*, **19**, 211 (1967).