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Tritium Fractionation on the Crystal Growth of Sodium Sulfate Decahydrate from Its Tritiated Aqueous Solution

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The fractionation of tritiated water (HTO) was examined during the crystallization of sodium sulfate decahydrate, $Na_2SO_4\cdot 10H_2O$, from a slightly supersaturated solution which contained a trace amount of tritium. No appreciable fractionation of HTO was found to occur in the crystallization under both stirred and unstirred conditions. The factors which may influence the degree of the fractionation were generally considered in connection with the studies by deuterated water. It was suggested that virtually all of the water of crystallization in sodium sulfate decahydrate should come from free water in its aqueous solution, and should integrate into the crystal in accordance with the volume-diffusion model. This model was supported also by the energetical consideration of the sodium ion in the crystallization.

The fractionation of deuterated water in inorganic salt hydrates has previously been examined, but the results are conflict as to the phase into which deuterated water is enriched.[1-3] It seems from these studies that the enrichment of the isotope in a liquid phase occurs in some salts, while there is the reverse or no fractionation in the other salts.

Recently, it has been reported by the present authors that tritiated water (HTO) is diluted in some inorganic salt hydrates during the crystallization from their aqueous solutions.[4] In this study, it has been proposed, on the basis of the crystal growth theory and an ionic process in a solution, that HTO is diluted in any salt hydrate, or else no fractionation of the isotope occurs.

It has been reported, however, that deuterated water is slightly enriched in the crystal of sodium sulfate decahydrate, $Na_2SO_4\cdot 10H_2O$.[1,3] In this connection, it seems interesting to examine the fractionation of HTO during the crystallization of the hydrated salt from a tritiated aqueous solution, since the results on the fractionation of HTO in copper sulfate pentahydrate and alum are parallel to that of deuterated water. In other words, HTO can be expected, according to the studies with deuterated water, to be enriched to some appreciable degree.

On the contrary, if HTO is diluted or not fractionated, the result can be explained in the same way as in our previous treatment,[4] assuming the mechanism of the crystallization of $Na_2SO_4\cdot 10H_2O$ from its aqueous solution as well as the behavior of water molecules during the crystallization.

Experimental

The sodium sulfate decahydrate was obtained from a commercial source and was purified by filtration with fiber-free-filter papers and by recrystallization. The solvent was twice-distilled water which contained a trace amount of tritiated water. The single crystal of $Na_2SO_4\cdot 10H_2O$ was grown from a slightly supersaturated tritiated aqueous solution at 29.65± 0.02°C by evaporating the solvent. The rate of solvent evaporation was adjusted in such a way that the relative supersaturation of the solution could be kept below *ca.* 2×10^{-3} during the crystallization.

The single crystals were thus obtained from both stirred and unstirred solutions under identical conditions unless otherwise stated. The crystal from a stirred solution was obtained by growing a seed attached to a copper wire which was rotated to give sufficient agitation.

Water from both the mother liquid and the hydrated single crystal was recovered by heating them until no further dehydration was observed under identical conditions. The tritium content in the water of crystallization was then compared with that in the corresponding mother liquid by analyzing the activity of tritium, as was described in a previous paper.[4]

Results and Discussion

The separation factor, S, of HTO for the equilibrium between solid and liquid phases has been given in a previous paper as follows:[4]

$$S = N_s/N_l, \tag{1}$$

where N_s and N_l are the mole fractions of HTO in the solid and liquid phases respectively. Table 1 gives the separation factor, S, together with the net counts per minute (cpm) coming from tritium; these counts are in proportion to N_s and N_l respectively.

TABLE 1. SEPARATION FACTOR, S, OF HTO DURING THE CRYSTALLIZATION OF $Na_2SO_4\cdot 10H_2O$ FROM A SOLUTION AT 29.65±0.02°C

The condition of mother liq.	Net cpm of tritiated water[a]		Separation factor (S)[b]
	Mother liq. (N_l)	Crystal (N_s)	
Unstirred	31535±146	31615±132	1.003±0.005
Stirred	33260±127	33273± 87	1.000±0.004

a) Each sample water was 0.1 g, and its cpm was measured using a counter of 35% efficiency.

b) The accuracy of the value of S is indicated in terms of the probable error.

It may be seen from Table 1 that no practical fractionation of HTO occurs during the crystallization of $Na_2SO_4\cdot 10H_2O$ from either the stirred or the unstirred solution.

Relation between the Present Data and Those of Other Workers. The data so far determined on the frac-

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

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

3) E. Uusitalo, *Suomen Kemistilehti*, **B31**, 362 (1958).

4) H. Tanaka and H. Negita, This Bulletin, **43**, 3079 (1970).

tionation of heavy water in $Na_2SO_4 \cdot 10H_2O$ are reproduced in Table 2.

TABLE 2. FRACTIONATION OF HEAVY WATER ON CRYSTALLIZATION OF $Na_2SO_4 \cdot 10H_2O$ FROM A SOLUTION

Heavy water (mol%)	Temp. of crystn. (°C)	Rate of crystn.	Separation factor (S)
D_2O (10)	26.5—25.5	Rapid	1.014[a]
D_2O (0.1, 1.0)	4, 25	Slow	1.001, 1.002[b]
HTO ($\sim 10^{-7}$)	29.65	Very slow	1.000, 1.003

a), b) Taken from Refs. 1 and 3 respectively.

Our results are in good agreement with those of Uusitalo,[3] but are discordant with the results of Johansson and Holmberg.[1] In the study of Johansson and Holmberg, however, a large amount of the crystal was grown from a 200-m*l* solution by cooling the solution at a rather rapid rate. Moreover, as the mother liquid a solution containing about 10 mole% of D_2O was used. These experimental conditions may allow an increasing ambiguity in the results or give results discordant with ours, as may be expected from the following considerations:

(1) It seems in general that the separation factor should be sensitive to the temperature of crystallization.[5]

(2) There is an increasing inclusion of the mother liquid into the growing crystal in the case of crystallization from a highly supersaturated solution.

(3) In the case of the fractionation of the isotope in the crystal, the mother liquid is subject to a reverse isotope effect.[6]

(4) When the mother liquid contains as much as 10 mole% of D_2O of heavy water, its behavior should be different from that of the liquid which is not enriched in D_2O. This situation will in turn complicate the problem.

Accordingly, it seems that each result listed in Table 2 is correct under the corresponding experimental conditions, although there may be some ambiguity unless the experimental conditions are strictly controlled. It will be worthwhile to use the present data of the fractionation of HTO in understanding the process of the crystal growth of $Na_2SO_4 \cdot 10H_2O$.

Estimation of the Fraction of Free Water Molecules in the Solution. A number of studies have been made of the determination of the hydration numbers of the Na^+ ion; the results so far reported vary depending upon the methods of determination. It is assumed in the present case that the Na^+ ion is surrounded, on the average, by four water molecules.[7]

The lifetime of the hydrated species has been found to be extremely short at room temperature, *i.e.*, *ca.* 10^{-9} sec, as evidenced by the relaxation technique.[8] Neglecting the hydration of the sulfate ion in the concentrated aqueous solution of Na_2SO_4,[9] it can be assumed that Na^+ and SO_4^{2-} ions enter the crystal practically independently of the water as well as of its isotopic concentration. The relaxation time of the Na^+ ion for entering into the crystal, τ, is expressed as follows:

$$\tau = (\boldsymbol{h}/\boldsymbol{k}T) \exp (E/\boldsymbol{k}T), \qquad (1)$$

where

$\boldsymbol{h}$ = Planck's constant,

$\boldsymbol{k}$ = the Boltzmann constant,

T = the absolute temperature, and

E = the activation energy of the cation for entering into the crystal from a solution, the minimum value of which has been assessed by Bennema to be *ca.* 10 kcal/mol.[10]

Accordingly, τ is estimated to be larger than *ca.* $10^{-5.5}$ sec at around room temperature. It follows that any water molecule in the vicinity of the Na^+ ion can reside in its hydration sphere only for an instant when the cation is fixed into the crystal.

Although intimate ion pairs may result at a high concentration of the Na_2SO_4 aqueous solution,[11] the lifetime of the species is also found to be very short, making it possible to treat it as separated ions. Moreover, it has been suggested by Samoilov that the Na^+ ion should migrate in the solution with almost no relation to the water in the vicinity.[9] It follows from the preceding argument that the water of crystallization in $Na_2SO_4 \cdot 10H_2O$ should practically result from free water molecules in the solution; that is, the species of the growth unit should be Na^+, SO_4^{2-}, and H_2O.

Calculation of Separation Factor in the Case of the Crystal Growth by a Surface-diffusion Mechanism. It has been reported in a previous paper that the separation factor, S, can be calculated on the basis of the ionic process in a solution and on the basis of the crystal-growth theory from a solution.[4] In the case of the crystal growth by a surface-diffusion mechanism, the rate of integration of a free water molecule into the crystal has been given by:

$$R = \alpha \Omega N_0 (\boldsymbol{k}T/2\pi m)^{1/2} (\sigma^2/\sigma_1) \tanh (\sigma_1/\sigma) \qquad (2)$$

where

α = the correction factor,

Ω = the volume of a growth unit in the crystal,

N_0 = the equilibrium concentration of growth units per cm^3 in the solution,

m = the mass of a growth unit,

σ = the relative supersaturation, and

σ_1 = the parameter.

In exactly the same manner as before, the R_{HTO}/R_{H_2O} ratio is obtained in the case of the crystal growth with an essential process of a surface diffusion of growth

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[5] Very recently it has been found by the present authors that the separation factor is considerably influenced by the temperature in the case of the crystallization of alum from a solution. This finding will be presented in detail elsewhere.

[6] In the present crystaplization, only *ca.* 1.5—2 g of the salt hydrate were obtained from a large amount of the mother liquid (*ca.* 800 g); thus, it may be possible to disregard this effect.

[7] H. G. Hertz, *Angew. Chem. Int. Ed. Engl.*, **9**, 124 (1970).

[8] F. Basalo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York (1967), Chap. 3.

[9] O. Ya. Samoilov, "Structure of Aqueous Electrolyte Solutions and the Hydration of Ions," Consultants Bureau Enterprises, Inc., New York (1965), Chap. 5.

[10] P. Bennema, Thesis, The Technical University of Delft (1965).

[11] D. R. Rosseinsky, *J. Chem. Soc.*, **1962**, 785.

units as follows:

$$R_{\mathrm{HTO}}/R_{\mathrm{H_2O}} = 0.949, \tag{3}$$

where $R_{\mathrm{HTO}}/R_{\mathrm{H_2O}}$ is the ratio of the integration of HTO into the crystal to that of H_2O molecules. Accordingly, the separation factor, S, in $Na_2SO_4 \cdot 10H_2O$ in the case of the surface-diffusion model can be simply calculated to be 0.949, since all of the water molecules of crystallization in $Na_2SO_4 \cdot 10H_2O$ can reasonably be assumed to result from free water in the solution, as has been described above. The preceding argument thus allows us to expect a considerable dilution of HTO in the crystal if the crystal grows by the surface-diffusion mechanism.

Calculation of Separation Factor on the Basis of a Volume-diffusion Mechanism of the Crystal Growth. If we adopt a volume-diffusion model for the growth from a solution in which a growth unit is directly transported from the solution to the kink without any surface diffusion,[10,12] the rate of the crystal growth is given by:

$$R = \{2\pi\lambda\varepsilon\beta DN_0\Omega kT/19\gamma ax_0)\}\sigma^2, \tag{4}$$

where

λ = the mean distance between one equilibrium position and a neighboring one in the solution,
ε = the measure of the interacting spirals,
β = the retarding factor,
D = the volume-diffusion constant,
γ = the edge free energy of a step with the length of a,
a = the shortest distance between growth units, and
x_0 = the mean distance between the kinks.

It follows from Eq. (4) that the $R_{\mathrm{HTO}}/R_{\mathrm{H_2O}}$ ratio is equal to the $D_{\mathrm{HTO}}/D_{\mathrm{H_2O}}$ ratio, where $D_{\mathrm{HTO}}/D_{\mathrm{H_2O}}$ is the ratio of the diffusion constants of HTO to H_2O molecules in a solution. When the crystal is grown from a well-stirred solution, the $D_{\mathrm{HTO}}/D_{\mathrm{H_2O}}$ ratio becomes unity, giving no fractionation of HTO during the crystallization of $Na_2SO_4 \cdot 10H_2O$. In the case of the crystallization from an unstirred solution, the $R_{\mathrm{HTO}}/R_{\mathrm{H_2O}}$ ratio can also be given by unity, since the value of D seems to be practically independent of the hydrogen isotope of the water molecules.[9]

Accordingly, it follows that no practical fractionation of HTO can be expected to occur during the crystallization of $Na_2SO_4 \cdot 10H_2O$ from either a stirred or an unstirred solution. It should be noted here that the calculation of the value of S on the basis of the volume-diffusion model leads to a satisfactory agreement with the present experimental results. That is, this argument implies that the crystal of $Na_2SO_4 \cdot 10H_2O$ grows by the volume-diffusion mechanism. This implication seems quite interesting in that the volume-diffusion mechanism has been proved for the first time to play an essential role in the crystallization of $Na_2SO_4 \cdot 10H_2O$, although the mechanism was proposed a long time ago and has been discussed generally from a theoretical point of view.[12-14]

The Relation between the Possible Volume-diffusion Mechanism and the Treatment by Bennema. According to Bennema,[12] the mean displacement of a growth unit on the crystal surface, x_s, is given by:

$$x_s = a\exp\{(E_{deads} - E_{sdiff})/2kT\} \tag{5}$$

where a is the shortest distance between neighboring growth units in the crystal, where E_{deads} is the activation free energy for leaving the surface, and where E_{sdiff} is the activation free energy for making a diffusion jump from one equilibrium position to a neighboring one on the surface. The volume-diffusion mechanism can be assumed to play an essential role in the growth of ionic crystals when $a \gtrsim x_s$, *i.e.*, $E_{sdiff} \gtrsim E_{deads}$, since growth units come practically to enter the crystal without any surface diffusion in this case.

The $E_{sdiff} \gtrsim E_{deads}$ condition can be met if the concept of Samoilov as to the hydration of the Na^+ ion is adopted.[9] That is, the transfer of the ion practically without any hydration water in a solution leads to a considerable decrease in the dehydration activation free energy for entering into the surface, E_{deh}, and thus to much smaller values of E_{deads}. It is reasonable to assume, in this case, that E_{deh} should be replaced by the activation free energy of the ion for a diffusion jump in a solution, E_a.

It can be estimated that E_{deads} is equal to 4.2 kcal/mol or somewhat greater, and that E_{sdiff} ranges between 5 and 10 kcal/mol.[10] Accordingly, the possible energy diagram of the growth unit (Na^+ ion) can be given as in Fig. 1.

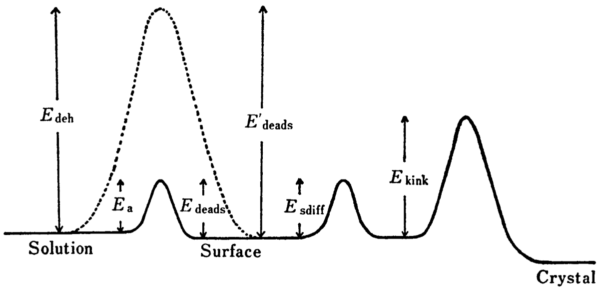

Fig. 1. The proposed energy diagram of Na^+ ion for entering into the crystal of $Na_2SO_4 \cdot 10H_2O$ from its aqueous solution.

In Fig. 1, E'_{deads} is the activation free energy for the Na^+ ion to leave the surface, which is needed if the ion must be dehydrated before entering into the surface (the curve is shown by a dotted line). This model has been adopted by Bennema in discussing the growth of some ionic crystals from their aqueous solutions.[10] Although the energetical consideration is rather ambiguous at this state, it can at least be stressed that the value of E_{deh} is as large as 10—30 kcal/mol, while the value of E_a is only *ca.* 4.2 kcal/mol.[10]

It can be concluded from the preceding discussion that the crystal growth of $Na_2SO_4 \cdot 10H_2O$ from its aqueous solution probably occurs by the volume-diffusion mechanism.

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[13] W. K. Burton, N. Cabrera, and F. C. Frank, *Phil. Trans. Roy. Soc.*, **A243**, 299 (1951).
[14] A. A. Chernov, *Soviet Phys. Usp.*, **4**, 116(1961).