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The Fractionation of Tritiated Water in Several Hydrated Chlorides

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The fractionation of tritiated water (HTO) on the crystallization of various hydrated sulfates from their aqueous solutions has been reported in our recent papers.[1,2] It may also be worthwhile to examine such a fractionation in other hydrated salts, because more data seem to be necessary in order for us to study the fractionation in a systematic way. In the present investigation, hydrated chlorides of cobalt, strontium, and barium have been chosen for study.

The results have been discussed on the basis of the crystal-growth mechanism and an ionic process in the solution in a way similar to that described in a previous paper.[1] Furthermore, other factors such as the dehydration temperature of the chloride have been taken into account. For this purpose, thermal analyses, *i.e.*, the DTA and TGA of the hydrated chlorides, were studied, since no exact dehydration temperatures have yet been determined, as far as we know.

Experimental

Crystal Growth. The chlorides, of commercial origin, were purified by recrystallization. The purified salts were put into the solvent, which consisted of twice-distilled water containing a trace of tritiated water (HTO). The well-developed single crystal of the hydrated chloride was grown from a very slightly super saturated aqueous solution by evaporating the solvent gradually. At the same time, the temperature of the solution was lowered in a narrow range in order to suppress the formation of stray crystals. The temperature ranges were 38.3—37.9°C for $CoCl_2 \cdot 6H_2O$, 40.3—39.7°C for $SrCl_2 \cdot 6H_2O$, and 37.7—37.3°C for $BaCl_2 \cdot 2H_2O$.

Recovery of Water and Analysis of the β-Activity. Water from both the mother liquor and the hydrated single crystal was recovered by heating them under identical conditions. The β-activity of the sample water was measured with a liquid scintillation counter, as has been described in a previous paper.[1]

Thermal Analysis. TGA and DTA were carried out simultaneously with a thermal analyzer, Model 8002 TG-DTA, of the Rigaku Denki Co., Ltd., using a sample of *ca.* 20 mg and heating it at the rate of 5°C/min.

Results and Discussion

The separation factor of HTO, S, on the crystal growth of a hydrated salt from a slightly supersaturated aqueous solution is given as follows:

$$S = N_s/N_l, \qquad (1)$$

where N_s and N_l are the mole fractions of HTO in the water of crystallization and in the mother liquor respectively. Table 1 gives the S values for the hydrated chlorides, together with the net cpm due to HTO in the water. It can be seen that an appreciable dilution of HTO occurs in the crystalline water of the chlorides. The dilution in $SrCl_2 \cdot 6H_2O$ may be compared with the S value of deuterated water (mostly HDO), which has been determined to be 0.977± 0.005 by Barrer and Denny.[3]

TABLE 1. THE SEPARATION FACTOR, S, OF HTO FOR HYDRATED CHLORIDES

Crystal	Net cpm of HTO[a] N_s	Net cpm of HTO[a] N_l	S_{obsd}
$CoCl_2 \cdot 6H_2O$	23688±188	24244±229	0.977±0.008
$SrCl_2 \cdot 6H_2O$	20328± 88	21472± 83	0.947±0.004
$BaCl_2 \cdot 2H_2O$	17929±191	19311±115	0.928±0.008

a) Averaged for several measurements using 0.1 g of the sample water recovered from the hydrated crystal of 2—3 g.

It was reported in a previous paper that the appreciable dilution of HTO in the hydrated crystal might be attributed to the surface-diffusion model of the crystal growth and to an ionic process in an aqueous solution.[1] The S value of the free water can thus be approximately calculated as 0.949 ($=(18/20)^{1/2}$) for the surface diffusion, provided that a possible fractionation of HTO in the hydration water of an ion from bulk water is disregarded.[4]

According to this treatment, the S value for $CoCl_2 \cdot 6H_2O$ can be derived as *ca.* 0.975, assuming that half of the hydration water of $Co(OH_2)_6^{2+}$ in the solution becomes free to integrate into the crystal.[1] On the other hand, it can be assumed in the cases of $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ that practically all of the water of crystallization comes from free water in the solution, because the half-lives, τ, of $Sr(OH_2)_6^{2+}$ and $Ba(OH_2)_6^{2+}$ in the solution[6] are much smaller than the relaxation times of these ions needed to integrate themselves into the crystal from the solution.[7] Accordingly, the S values for $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ are

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[1] H. Tanaka and H. Negita, This Bulletin, **43**, 3079 (1970).

[2] H. Tanaka, *J. Sci. Hiroshima Univ., Ser. A*, **36**, 31 (1972).

[3] R. M. Barrer and A. F. Denny, *J. Chem. Soc.*, **1964**, 4677.

[4] The disregard of the fractionation may be allowable in the present study, because no appreciable fractionation or a slight enrichment, if at all, in the hydration water seems to result.[5]

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[6] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

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

TABLE 2. THE CALCULATED S VALUE TOGETHER WITH THE τ, r_c, AND T_d VALUES

Crystal	S_{calc}	τ (sec)[a]	r_c (Å)	T_d (°C)
$CoCl_2 \cdot 6H_2O$	0.975	10^{-6}	0.72	185
$SrCl_2 \cdot 6H_2O$	0.949	10^{-9}	1.13	145
$BaCl_2 \cdot 2H_2O$	0.949	$10^{-9.5}$	1.35	120

a) Taken from Ref. 4.

derived as *ca.* 0.949 by means of the surface-diffusion model. Table 2 gives the estimated S values, together with the half-lives of the hydrated cations, τ.

It may be noticed here that the observed S values are in good agreement with the estimated ones for $CoCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot 6H_2O$, but not for $BaCl_2 \cdot 2H_2O$. Although the cause of the discrepancy can not be ascertained at this stage, it is interesting to note that the observed S value decreases with an increase in the cationic radius, r_c, of the chloride (*cf.* the fourth column of Table 2). The increase in the radius leads to a hydrated ion with a shorter half-life in the solution,[8] which in turn gives more free water in the process of diffusion onto the crystal surface.[9] The S value should thus decrease with an increase in the mole fraction of free water in the solution according to the present assumption that free water is largely responsible for the dilution of HTO in the crystal.

The too small S value for $BaCl_2 \cdot 2H_2O$ seems likely to be caused by the following factors of (1) and/or (2):

(1) As has been pointed out in Ref. 1, the minimum S value estimated should be regarded as an approximate one, because some approximation and assumption are included in the derivation. A small deviation of the estimated value from the observed one seems to be inevitable, as was the case with the few other inorganic hydrates.[1,10] From the viewpoints of the crystal-growth mechanism and the ionic process, however, the direction of the dilution may be significant in our study.

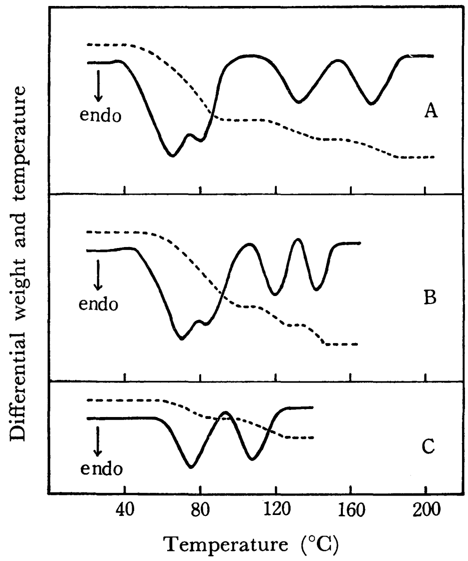

Fig. 1. Curves of the simultaneous DTA and TGA for the dehydration of the hydrated chlorides of cobalt (A), strontium (B), and barium (C).
——: DTA, ----: TGA, and endo: endothermic

(2) The dehydration temperature, T_d, of the barium chloride dihydrate is considerably lower than those of the other chlorides (*cf.* the last column of Table 2), as may be seen from the DTA and TGA curves in Fig. 1. This fact shows that the bonding of the crystalline water is relatively weak; this might be related to the too small S value, since the content of a heavier isotope in a given chemical species is known to decrease as the bonding becomes weaker in the case of an exchange reaction of isotopes.

We still believe that the major cause of the observed dilution in the chloride is the surface-diffusion mechanism of the crystal growth, since the possible enrichment, if any, of HTO in the hydration water of the Ba^{2+} ion in the solution seems to be negligible.[5]

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[10] H. Tanaka, T. Kado, and H. Negita, *ibid.*, **45**, 3342 (1972).