BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(7), 1793—1794 (1974)

Tritium Fractionation in the Crystallization of Aluminum Alums from Their Aqueous Solutions

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(Received November 12, 1973)

Synopsis. The tritium fractionation in the crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ from a solution was found to be larger than those in $NaAl(SO_4)_2 \cdot 12H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$. This fact was discussed in terms of the proton exchange between NH_4^+ and H_2O.

In previous studies,[1] the fractionation of tritiated water (HTO) has been investigated in the crystallization of a number of hydrated crystals. It was found that HTO is generally diluted with crystallization water to a small percentage. It seems to be of some importance to examine the behavior of NH_4^+ in the tritium fractionation in $NH_4Al(SO_4)_2 \cdot 12H_2O$, with reference to the results in $NaAl(SO_4)_2 \cdot 12H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$.

Experimental

The aluminum alums of commercial origin were purified by recrystallization. The large single crystal of the salt was grown from a slightly supersaturated aqueous solution containing a trace of HTO at around 20 °C.

The water from the single crystals of sodium- and ammonium alums was recovered by heating them at *ca.* 300 °C in a stream of nitrogen gas and at *ca.* 50 °C *in vacuo* respectively. The water from the mother solution was recovered through distillation and subsequent dehydration. The tritium radioactivity was compared between the dehydrated water and the mother liquid as has been described in a previous paper.[1] Simultaneous TGA and DTA were carried out for the dehydration of the three kinds of alums with a thermal analyzer, M8002 TG–DTA, of the Rigaku Denki Co. Ltd., at the rate of 5 °C/min in an atmosphere of nitrogen.

Results and Discussion

The separation factor, S, of HTO for the crystallization of a hydrated salt from an aqueous solution can be given as $S = N_s/N_l$, where N_s and N_l are the net count rates for a 0.1 g portion of water recovered from the solid and liquid phases respectively.[1] Table 1 gives the separation factors, S, for the aluminum alums. We see that there is only a small percentage of dilution of HTO in the water of crystallization of sodium- and potassium aluminum alums,[2] as is the case with many inorganic hydrated crystals.[1]

TABLE 1. THE SEPARATION FACTOR, S, OF HTO FOR ALUMS

Crystal	Net count rate (cpm) of HTO[a]		$S(N_s/N_l)$
	N_s	N_l	
$NaAl(SO_4)_2 \cdot 12H_2O$	19419	20076	0.967 ± 0.006
$KAl(SO_4)_2 \cdot 12H_2O$	26426	27097	0.975 ± 0.004[b]
$NH_4Al(SO_4)_2 \cdot 12H_2O$	13121	14061	0.933 ± 0.006

a) Averaged from 5—6 independent experiments for 0.1 g of water with 35% efficiency.
b) From Ref. 2.

The fractionation in $NaAl(SO_4)_2 \cdot 12H_2O$ can be explained by a mechanism similar to that in $KAl(SO_4)_2 \cdot 12H_2O$. On the contrary, a remarkable dilution of HTO is found in $NH_4Al(SO_4)_2 \cdot 12H_2O$. It seems that hydrogen atoms in the NH_4^+ ion are responsible for the considerable dilution, because the dilution due to the crystallization water in sodium- and potassium aluminum alums is found to be small.

It can be assumed here that the dilution in the crystallization water of $NH_4Al(SO_4)_2 \cdot 12H_2O$ is equal to that in $KAl(SO_4)_2 \cdot 12H_2O$, This is supported by the facts that (1) the crystal-growth mechanism of these alums is identical,[3] (2) the K^+ and NH_4^+ ions have similar ionic radii and viscosity-B coefficients,[4] and (3) these alums give very similar DT–TGA curves for the dehydration, as is shown in Fig. 1.

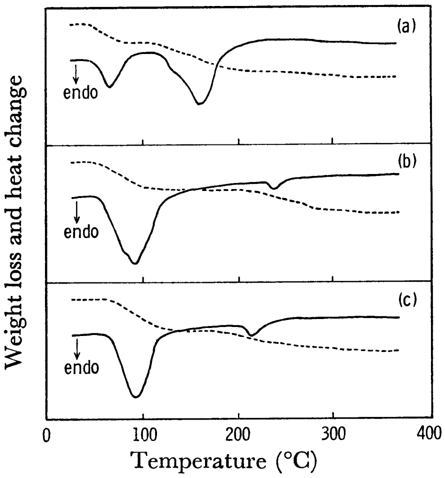

Fig. 1. DTA (——) and TGA (----) diagrams for dehydration of alums.
(a): $NaAl(SO_4)_2 \cdot 12H_2O$, (b) :$KAl(SO_4)_2 \cdot 12H_2O$, (c): $NH_4Al(SO_4)_2 \cdot 12H_2O$.

It is well-known that the proton-exchange reaction occurs readily in the aqueous solution of NH_4^+:[7]

$$HTO + NH_4^+ \rightleftharpoons H_2O + NH_3T^+ \qquad (1)$$

In Eq. (1), tritium may be diluted in NH_4^+ according to the theory of isotope effect in an equilibrium reaction, because the proton in NH_4^+ is labile in comparison with that in H_2O.[8] It follows that tritium is diluted in the NH_4^+ of the crystal of $NH_4Al(SO_4)_2 \cdot 12H_2O$ grown from the aqueous solution.

Accordingly, a considerable dilution of tritium in the dehydrated water may become possible since a proton-exchange reaction is expected to occur between NH_4^+ in the amorphous $NH_4Al(SO_4)_2$ and dehydrated water during the vacuum dehydration, as has been suggested for the dehydration of $(COOH)_2 \cdot 2H_2O$ by Okazaki and Takemura.[9,10]

In conclusion, the too small S value for $NH_4Al(SO_4)_2 \cdot 12H_2O$ compared with those for the other alums can be explained qualitatively in terms of the proton-exchange reaction between NH_4^+ and H_2O in both the aqueous solution and the vacuum dehydration.

The authors wish to express their thanks to Dr. Osamu Yamamoto for his help in analysing the activity of tritium.

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