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Oxygen Exchange between Arsenate Ions and Water of Crystallization in the Course of Hydration and Dehydration of Disodium Hydrogen Arsenate and Sodium Dihydrogen Arsenate

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Oxygen exchange between arsenate ions and crystal water in the course of hydration of anhydrous salt with water vapor and subsequent dehydration of the resulting hydrate has been studied with disodium hydrogen arsenate and with sodium dihydrogen arsenate. There is a remarkable difference in the exchange behavior between the anhydrous salt prepared by dehydration *in vacuo* at room temperature and that prepared at higher temperatures. In the former, the degree of exchange increases with increasing molar ratio of the reactants(arsenate to water), while in the latter, it is independent of the molar ratio. In the exchange reactions of the anhydrous salt prepared at higher temperatures, the number of exchangeable oxygen atoms of an arsenate ion is found to be 0.5 (that is, one atom for two arsenate ions) for disodium hydrogen arsenate, and 4 for sodium dihydrogen arsenate.

In previous publications,[1-3] we reported on the studies of deuterium and oxygen-18 exchange reactions between crystal water and anhydrous salt(or lower hydrate) in the course of hydration of anhydrous salt with water vapor and subsequent dehydration of the resulting hydrate. The characteristics of these reactions are: 1) With crystalline anhydrous salt prepared by dehydration at higher temperatures(*ca.* 100 °C), the amount of anhydrous salt which takes part in the exchange reaction is always equivalent to the amount of water used for hydration. On the other hand, with highly dispersed anhydrous salt prepared by dehydration *in vacuo* at room temperature, the amount of anhydrous salt which takes part in the exchange reaction increases, for a given amount of water, with increasing amount of anhydrous salt used. 2) In the exchange reactions of oxalic acid,[1] copper sulfate monohydrate,[2] sodium dihydrogen phosphate and racemic acid,[3] all the hydrogen atoms which are easily replaced by the hydrogen atoms of water in aqueous solutions are exchangeable for those of crystal water. The oxygen-18 exchange of copper sulfate monohydrate has shown that scrambling of the "fifth" water molecule of copper sulfate pentahydrate with the remaining four molecules of crystal water occurs in the process of hydration and dehydration.[2] In these exchange reactions, exchange equilibrium is reached during the process of hydration and dehydration. Thus, with regard to the exchangeability of hydrogen or oxygen atom, the exchange reactions of anhydrous salt with crystal water seem to be analogous to the exchange reactions in solution. The present paper describes the oxygen exchange reactions of arsenate ions with crystal water in the course of hydration and dehydration, in one of which the exchangeability of arsenate oxygen has been found to differ greatly from that of arsenate oxygen in aqueous solutions.

Experimental

Materials. Disodium hydrogen arsenate heptahydrate(Special grade, JIS) was used without further purification. Sodium dihydrogen arsenate monohydrate was prepared as follows. Arsenic acid(60%, chemically pure) was neutralized to its first neutralization point with a sodium hydroxide solution(Special grade, JIS). The salt obtained on concentrating the solution was recrystallized twice from water. Oxygen-18 water(excess density *ca.* 800γ) was obtained by the fractionation of water. Its deuterium content was normalized by repeated exchange with ammonium chloride. It was refluxed with alkaline permanganate and distilled twice.

Preparation of Anhydrous Salts. Two kinds of anhydrous salts were studied both for disodium hydrogen arsenate and for sodium dihydrogen arsenate. One, probably in a highly dispersed state, was prepared by dehydration *in vacuo* at 30 °C. The other, crystalline, was prepared by dehydration to a constant weight at higher temperatures under the atmospheric pressure. In practice, the hydrates were partially dehydrated *in vacuo* at room temperature and then dehydrated and annealed at higher temperatures(95 °C for disodium hydrogen arsenate, 70 °C for sodium dihydrogen arsenate). To check the composition of the arsenates obtained, a portion of the anhydrous salt was heated to yield

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[1] N. Okazaki and E. Takemura, This Bulletin, **34**, 977 (1961).
[2] N. Okazaki, A. Okumura and K. Nakagawa, *ibid.*, **34**, 983 (1961).
[3] N. Okazaki and A. Okumura, *ibid.*, **34**, 985 (1961).

pyro- or meta-arsenate, and the water released was collected and weighed. The amount of the water was in satisfactory agreement with the stoichiometric amount.

Procedure. The procedure was the same as that used earlier.[1] A weighed amount of anhydrous salt was hydrated in a vacuum system at a constant temperature with heavy water vapor. After the completion of hydration, which took about 10 hours, the hydrate was dehydrated by condensing the water vapor in a trap cooled with a dry ice-ethanol bath. The water obtained was purified thoroughly, and its excess density was measured by the flotation method. The excess density of oxygen-18 water is, to a good approximation, proportional to its oxygen-18 atom fraction in excess of the natural.

Results and Discussion

The reaction can be formulated as follows:

$$(\mathrm{Na,\ H})_3\mathrm{AsO}_4 + \mathrm{H_2{}^{18}O} \rightleftarrows \text{Hydrate} + \text{Anhydrous salt} \rightleftarrows (\mathrm{Na,\ H})_3\mathrm{AsO_3{}^{18}O} + \mathrm{H_2O}.$$

The balance of oxygen-18 atoms in this reaction is,

$$M_\mathrm{w}D_\mathrm{i} = M_\mathrm{w}D_\mathrm{f} + n_\mathrm{O}M_\mathrm{s}'k_\mathrm{O}D_\mathrm{f}, \qquad (1)$$

where D_i and D_f: the excess oxygen-18 atom fractions of water before hydration and after dehydration respectively,

M_w: the number of moles of water used for the hydration,

M_s': the number of moles of the arsenate taking part in the exchange reaction,

n_O: the number of exchangeable oxygen atoms in an arsenate ion,

k_O: the oxygen-18 partition coefficient between the arsenate and the hydrate water ($k_\mathrm{O}\simeq 1$).

Eq. (1) can be rewritten as:

$$(D_\mathrm{i}-D_\mathrm{f})/D_\mathrm{f}k_\mathrm{O} = \Delta D/D_\mathrm{f}k_\mathrm{O} = n_\mathrm{O}(M_\mathrm{s}'/M_\mathrm{w}). \qquad (2)$$

As the anhydrous salt was always used in excess, a part of it is left unhydrated even after the completion of hydration. If, of the M_s moles of the anhydrous salt used, M_s' moles take part in the exchange reaction, Eq. (2) can be written as:

$$\Delta D/D_\mathrm{f}k_\mathrm{O} = n_\mathrm{O}(M_\mathrm{s}'/M_\mathrm{s})(M_\mathrm{s}/M_\mathrm{w}). \qquad (3)$$

Accordingly, if we plot the result of the exchange reaction, taking $\Delta D/D_\mathrm{f}k_\mathrm{O}$ as ordinate and $M_\mathrm{s}/M_\mathrm{w}$ as abscissa, the slope of a line drawn through the plotted point and the origin gives the value of $n_\mathrm{O}(M_\mathrm{s}'/M_\mathrm{s})$, and hence of $(M_\mathrm{s}'/M_\mathrm{s})$.

As a special case, when the anhydrous salt and the hydrate water take part in the exchange reaction in the equivalent proportion corresponding to the formula $(\mathrm{Na,H})_3\mathrm{AsO}_4\cdot m\mathrm{H_2O}$, $mM_\mathrm{s}'=M_\mathrm{w}$. Eq. (2) then becomes:

$$\Delta D/D_\mathrm{f}k_\mathrm{O} = n_\mathrm{O}/m. \qquad (4)$$

In this case the value of $\Delta D/D_\mathrm{f}k_\mathrm{O}$ becomes independent of $M_\mathrm{s}/M_\mathrm{w}$. This situation is realized when the exchange reaction occurs exclusively in the reaction zone and the hydrate lattice.[1]

Disodium Hydrogen Arsenate. The results obtained with disodium hydrogen arsenate are shown in Fig. 1. Hydration was carried out at 20 °C with water vapor of *ca* 10 mmHg, and dehydration at 30 °C *in vacuo*. It will be seen that there is a qualitative difference in exchange behavior between the anhydrous salt prepared *in vacuo* at room temperature and that prepared at 95 °C. In the former case, the degree of oxygen exchange, $\Delta D/D_\mathrm{f}k_\mathrm{O}$, increases with increasing excess of the anhydrous salt. The line passing through the plotted points and the origin gives a slope ($=n_\mathrm{O}(M_\mathrm{s}'/M_\mathrm{s})$) of 1.71. If the value of n_O is taken to be 4, which is the case with the oxygen exchange of arsenate ions in aqueous solution, $M_\mathrm{s}'/M_\mathrm{s}=0.43$. That is, 43% of the anhydrous salt used takes part in the exchange reaction irrespective of the value of the molar ratio $M_\mathrm{s}/M_\mathrm{w}$. This fact suggests that the enhanced exchangeability of the anhydrous salt prepared at room temperature is the property of the anhydrous salt itself. In this case, the exchange reaction probably occurs mainly on the surface of the highly dispersed solid, $M_\mathrm{s}'/M_\mathrm{s}$ being a measure of surface-to-bulk ratio of the anhydrous salt.

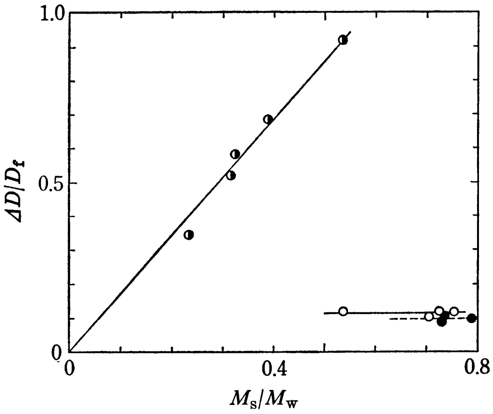

Fig. 1. Degree of exchange $\Delta D/D_\mathrm{f}$ as a function of the ratio of moles of anhydrous disodium hydrogen arsenate to moles of water, $M_\mathrm{s}/M_\mathrm{w}$. ◑, Oxygen exchange of the anhydrous salt prepared by dehydration *in vacuo* at 30 °C. ○: Oxygen exchange of the anhydrous salt prepared at 95 °C, ●: Deuterium exchange of the anhydrous salt prepared at 95 °C.

On the other hand, with the anhydrous salt prepared at 95 °C, the value of the degree of oxygen exchange, $\Delta D/D_\mathrm{f}k_\mathrm{O}$, is 0.1, independent of the values of $M_\mathrm{s}/M_\mathrm{w}$. The anhydrous salt and the hydrate water react with each other in a fixed proportion. From (4) we get:

$$n_\mathrm{O}/m = 0.1, \qquad (5)$$

where m is the number of crystal water of the hydrate formed on hydration of the anhydrous salt.

By using the deuterium exchange reaction in the process of hydration and dehydration, we can estimate the value of m.[3] For the deuterium exchange, an appropriate equation corresponding to (2) is

$$\Delta D/D_\mathrm{f}k_\mathrm{D} = M_\mathrm{s}'/2M_\mathrm{w}, \qquad (6)$$

where k_D is the deuterium partition coefficient between the arsenate and crystal water in the hydrate. The deuterium exchange of the anhydrous salt prepared at 95 °C was studied under the same conditions as those of the oxygen-18 exchange (Fig. 1). It will be seen that the values of $\Delta D/D_\mathrm{f}$ are independent of $M_\mathrm{s}/M_\mathrm{w}$. The anhydrous salt and the hydrate water take part in the exchange reaction in the stoichiometric proportion determined by the formula, $Na_2HAsO_4 \cdot mH_2O$. By using the relation, $mM_s' = M_w$, and the mean value of $\Delta D/D_f = 0.095$, Eq. (6) can be written as:

$$m = k_D/0.19. \tag{7}$$

The value of k_D was determined as follows. Disodium hydrogen arsenate labelled with deuterium was prepared by crystallization from HDO solution. The salt was dehydrated *in vacuo* at 25 °C to remove the crystal water. The anhydrous salt obtained was then heated to 200 °C to yield pyroarsenate. The excess density of the water obtained in each step was measured by the flotation method. The value of k_D is given by the ratio of the excess density of water obtained in the second step to that in the first step. Four determinations yielded a value $k_D = 0.78 \pm 0.01$.

The value of m is calculated to be 4.1 from Eq. (7). Tetrahydrate of disodium hydrogen arsenate has not been reported. Pentahydrate is the nearest to it in composition among the known hydrates of disodium hydrogen arsenate.[4] Thus, the deuterium and the oxygen-18 exchange reactions under the given conditions proceed by way of the formation of penta- or tetra-hydrate. From Eq. (5) we obtain $n_O = 0.5$ or 0.4, that is, in the oxygen-18 exchange reaction in question, the number of exchangeable oxygen atoms is 0.5 per arsenate ion, or an atom for two arsenate ions.

It may be suspected that the exchange reaction does not attain the exchange equilibrium during the process of hydration and dehydration. To check this point, the anhydrous arsenate, after being hydrated partially with heavy water vapor, was kept at a constant temperature for a definite time before dehydration. The conditions for the hydration and dehydration were the same as those shown in Fig. 1. Deuterium exchange as well as oxygen exchange was studied, the results being shown in Fig. 2. The exchange reaction does not proceed appreciably in the partially hydrated arsenate at 20 °C, but does so at 30 °C and 40 °C. The data at 30 °C were obtained by using the doubly labelled water $HD^{18}O$. In this case, both the deuterium and oxygen-18 exchange reactions can be studied in a single process of hydration and dehydration. After the dehydration, the deuterium and the oxygen-18 contents of the water were measured separately.

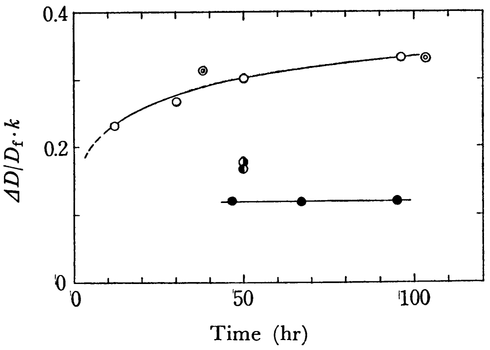

Fig. 2. Oxygen and deuterium exchange reactions in the partially hydrated disodium hydrogen arsenate. ●: Oxygen exchange; 20 °C, ◑: Oxygen exchange; 30 °C, ◐: Deuterium exchange; 30 °C, ○: Oxygen exchange; 40 °C, ◎: Deuterium exchange; 40 °C.

For the deuterium exchange it has been shown[1-3] that, during the process of hydration and dehydration, exchange equilibrium is established between the hydrate water and that part of the anhydrous salt which has taken part in the exchange reaction, and that the progress of the exchange reaction in the partially hydrated arsenate is due to the participation of fresh anhydrous arsenate which has not taken part in the exchange reaction. Fig. 2 shows that the progress of the oxygen-18 exchange keeps pace with that of the deuterium exchange. This suggests that also for the oxygen-18 exchange reaction exchange equilibrium is established during the process of hydration and dehydration, and that the progress of the exchange in partially hydrated arsenate is due to the participation of the fresh part of the anhydrous arsenate.

The number of exchangeable oxygen atoms in an arsenate ion, n_O, can also be calculated without the knowledge of the value of m. By dividing Eq. (2) by Eq. (6), we obtain:

$$k_D(\Delta D/D_f)_O/k_O(\Delta D/D_f)_D = 2n_O, \tag{8}$$

where the suffixes O and D refer to the oxygen and the deuterium exchange reactions, respectively. Here it has been assumed that $(M_s'/M_w)_D = (M_s'/M_w)_O$. The parallel progress of the oxygen and deuterium exchange reactions (Fig. 2) suggests the assumption to be probable. It is valid with doubly labelled water, since the oxygen and the deuterium exchange reactions are studied in a single process of hydration and dehydration. Fig. 2 shows that $(\Delta D/D_f)_O/k_O \simeq (\Delta D/D_f)_D/k_D$ for the experiments at 40 °C and 30 °C with doubly labelled water. Hence, $2n_O \simeq 1$, or $n_O \simeq 0.5$, in agreement with the result obtained above.

In the exchange reactions of the anhydrous salt prepared at room temperature, it has been shown that, assuming all four oxygen atoms of arsenate ion to be exchangeable, 43% of the anhydrous arsenate used takes part in the exchange reaction. If two of the four oxygen atoms are assumed to be exchangeable, 86% of the anhydrous arsenate should participate. However, the number of exchangeable oxygen atoms should not be smaller than 2, for then more than 100% of the anhydrous arsenate used should have taken part in the exchange reaction. Thus there is a remarkable difference in the number of exchangeable oxygen atoms between the crystalline and the highly dispersed anhydrous arsenate. In the latter, the ions would be rather loosely bound with each other, and the exchange reaction with adsorbed water or with hydrate water may be considered to be more or less analogous to the exchange reaction in solution. On the other hand, with the crystalline anhydrous arsenate, the exchange reaction would be controlled by the geometry of the crystal lattice of the anhydrous arsenate, and it is possible that the number of exchangeable oxygen atoms is also limited by the crystal structure of the anhydrous arsenate. In the absence of information on the crystal structures of the anhydrous and the

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[4] H. Menzel and W. Hagen, *Z. Anorg. Allgem. Chem.*, **233**, 209 (1937).

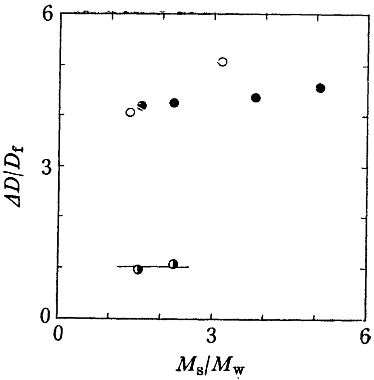

Fig. 3. Degree of exchange $\Delta D/D_f$ as a function of the ratio of moles of anhydrous sodium dihydrogen arsenate to moles of water, M_S/M_W. ○: Oxygen exchange of the anhydrous salt prepared *in vacuo* at 22 °C, ●: Oxygen exchange of the anhydrous salt prepared at 70 °C, ◑: Deuterium exchange of the anhydrous salt prepared at 70 °C.

hydrated forms of the arsenate, we cannot give a picture of hydration and dehydration, or an explanation of the number of exchangeable oxygen atoms.

Sodium Dihydrogen Arsenate. The results obtained with sodium dihydrogen arsenate are given in Fig. 3. For the anhydrous salt prepared *in vacuo* at 30 °C, hydration was carried out at 30 °C with water vapor of *ca* 16 mm, and dehydration at 30 °C *in vacuo.* For the anhydrous salt prepared at 70 °C, hydration was carried out at 22 °C with water vapor of *ca* 13 mm, and dehydration at 22 °C *in vacuo.* The characteristics of the exchange reaction of the crystal water may be seen, but the difference in behavior between the two kinds of anhydrous arsenate is not so well marked as in the case of disodium hydrogen arsenate. The values of $\Delta D/D_f$ for the anhydrous arsenate prepared at 70 °C increase with increasing M_s/M_w. From the results of deuterium exchange of the anhydrous arsenate prepared at 70 °C, the number of crystal water of the hydrate formed on hydration of the anhydrous salt, *m*, can be calculated by the relation:

$$m = k_D/(\Delta D/D_f)_D. \qquad (9)$$

where k_D is the deuterium partition coefficient between the dihydrogen arsenate ion and crystal water in the hydrate of sodium dihydrogen arsenate. This was determined as follows. $NaHDAsO_4 \cdot HDO$ was prepared by crystallization from HDO solution. The salt obtained was dehydrated *in vacuo* at 30 °C to separate the crystal water, and then the resulting anhydrous salt was heated at 350 °C to yield metaarsenate. k_D is given by the ratio of the deuterium atom fraction of the arsenate hydrogen, that is, that of the water obtained in the second step, to that of the crystal water. Three determinations yielded a value $k_D = 0.845 \pm 0.002$. By using this value and that of $\Delta D/D_f$ for the deuterium exchange (Fig. 3), *m* is calculated to be 0.85 from Eq. (9). The exchange reaction between the crystal water and the arsenate ion in sodium dihydrogen arsenate proceeds through the formation of monohydrate under the condition of the experiments.

By substituting the value of *m* obtained and the value of $\Delta D/D_f$ of the oxygen exchange (Fig. 3) in Eq. (4), the number of exchangeable oxygen atoms of sodium dihydrogen arsenate, n_O, is calculated to be 4.3 ± 0.1. In the exchange reaction of sodium dihydrogen arsenate, all four atoms of the arsenate oxygen are exchangeable. This is in strong contrast to the exchange reaction of disodium hydrogen arsenate, where one atom for two arsenate ions is found to be exchangeable.

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