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INTRACRYSTALLINE SITE PREFERENCE OF HYDROGEN ISOTOPES IN THE WATER OF CRYSTALLIZATION OF NICKEL SULFATE HEPTAHYDRATE

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The difference in hydrogen isotope distribution in different sites of the water of crystallization of $NiSO_4 . 7H_2O$ (the site preference) was determined. Six molecules of the water of crystallization are in the co-ordination sphere of nickel ion (site A), while the remaining one is bonded to sulfate ion through hydrogen bonding (site B). $NiSO_4 . 7H_2O$ was dehydrated fractionally in vacuum at 0°, and the isotopic ratio and the quantity of water for each fraction was measured. The rate process of dehydration was elucidated. The following results are obtained: (i) The dehydration is presented by the three zeroth-order rate processes which have different rate constants of dehydration. (ii) Two maxima exist in the isotopic ratio in the dehydration range, $F<0.710$. The site preference of hydrogen isotopes ($\delta D‰$) was concluded to be -20 for site A and +98 for site B, where the δD value was referred to the isotopic ratio of the mother liquor from which the crystal was grown.

Key words : Fractional dehydration, Fractional factor, Site preference.

Introduction

The difference in the isotopic partition of oxygen and hydrogen in the coordination sphere was investigated by a number of authors [1-4]. Furthermore, information on the fractionation of hydrogen and/or oxygen isotopes between crystals and their saturated solutions has also been accumulated [5-10]. Hamza and Epstein [11] estimated oxygen isotopic fractionation between the OH group and other oxygen sites in hydroxyl bearing silicate minerals and found that there is a significant difference in the $^{18}0/^{16}0$ ratio. Heinzinger and Maiwald [12] conducted a fractional dehydration experiment in order to determine the site preference of hydrogen and oxygen isotopes in the water of crystallization of $CuSO_4 . 5H_2O$. They concluded that D/H ratio of the water molecule bonded to sulfate ion through hydrogen bonding was higher than the D/H ratio of waters coordinated to the copper ion. Based on fractional dehydration experiments, Kita and Matsuo [13] concluded that water molecules in the coordination sphere of Cu^{2+} were depleted in deuterium by 32% and water molecules bound to SO_4^{-2} through hydrogen bonding were enriched by 22.6% compared with the mother liquor. In this paper, we will discuss the site preference of hydrogen isotopes in the water of crystallization of $NiSO_4 . 7H_2O$ applying the fractional dehydration technique.

The crystal structures of nickel sulfate heptahydrate and hexahydrate have been well established [14,15]. The structure of $NiSO_4 . 7H_2O$ suggests that there exists a significant difference in geometry and energetics with respect to hydrogen atoms in the crystal. The change in bonding and/or structure situation of the water of crystallization should, therefore, result in the isotopic site preference.

Experimental

Crystallization of nickel sulfate heptahydrate at 25°. Nickel sulfate hexahydrate, $NiSO_4 . 6H_2O$ (reagent grade) was dissolved in distilled water to prepare a supersaturated solution (15% excess with respect to $NiSO_4 . 7H_2O$). The solution was filtered into a stoppered conical flask. The flask was placed in a thermostated bath at 25 ±0.1° for about 10 days. The crystal formed in this way was not taken out of the solution before use since $NiSO_4 . 7H_2O$ loses one molecule of water very quickly to form $NiSO_4 . 6H_2O$.

Measurement of the D/H ratio for the bulk water of crystallization. A small crystal of $NiSO_4 . 7H_2O$ (about 20mg) was taken from the solution and was dried by pressing between filter papers. The crystal was put quickly in a previously weighed dehydration tube (Pyrex tube) fitted with a stopcock. The stopcock fitted tube was used in order to prevent any loss of water of crystallization during the weighing process. The dehydration tube, cooled externally by liquid nitrogen, was loaded to a high vacuum line and evacuated. The dehydrated water was first condensed in a trap cooled by liquid nitrogen and was then converted to hydrogen gas [16] by passing the water vapour through uranium metal at 750°. The dehydration scheme used was the same as that of Kita and Matsuo [13]. The volume of hydrogen gas was measured manometrically after complete collection of the gas with the help of a Toepler pump. The D/H ratio of the H_2 gas was determined by a mass spectrometer with dual inlet and collector system (Hitachi RMD).

The isotopic ratio is presented by the following equation:

$$D(‰) = \frac{(D/H)_{sample} - (D/H)_{standard}}{(D/H)_{standard}} \times 10^3$$

The D/H ratio of the mother liquor in equilibrium with the $NiSO_4 \cdot 7H_2O$ crystal is taken as the standard in this paper. The error in the δD measurements is ±1%.

Fractional dehydration. The schematic digram of the system for fractional dehydration used in this study is shown in Fig. 1. As shown in Fig. 2, the dehydration vessel was a glass tube 'A' with a short side tube 'B'. Part C was disconnected and 460.5mg of the crystal of $NiSO_4 \cdot 7H_2O$ taken out from the thermostat immediately before the experiment was placed in tube B. Part C was then connected with tube A in such a way that the opening of tube B was closed. The tube A was evacuated and after closing the stopcock, the whole system, i.e. the assemblage of tube A, B and part C was taken away from the evacuation line. The whole system was held by a clamp to cool the tube B by liquid N_2 for about an hour in order to condense the water vapour already present in the tube B.

Tube B was then opened by turning the ground joint. Tubes A and B were cooled by liquid N_2 for 20 mins. The crystal was then allowed to fall from tube B to tube A, very quickly and immediately the tube B was closed by turning the ground joint in the proper direction. The crystal was pulverized inside the tube A by means of a glass ball while cooling the glass tube A externally by liquid N_2 to prevent any loss and exchange of water during pulverization. The sample powder thus formed was placed thinly inside the glass tube A in order to check any temperature gradient during the dehydration process. The size distribution of $NiSO_4 \cdot 7H_2O$ powder could not be measured before dehydration. The dehydration system containing the sample powder was loaded again to the evacuation line through the ground joint. Glass tube A was evacuated completely to 10^{-3} torr at liquid N_2 temperature. Glass tube A was then immersed in an ice-bath maintained at 0°. The water collection was made without interuption by using the two-way system shown in Fig. 1, so that the sample tube prepared for the collection of dehydrated water in one limb could be evacuated while the condensation of dehydrated water in the other limb was going on. The collected water of each fraction was introduced to the conversion line including the uranium furnace to reduce to H_2 gas. The quantity of water collected in a fraction during fractional dehyderation was sometime as small as 1.6 mg.

Results and Discussion

Bulk water of crystallization. Reports from the study made by Barrer and Denny [6] and Matsuo *et al.* [17] reveal that the D/H ratios of hydrated crystals are mostly lower than those of the mother liquor in equilibrium with the crystals. Matsubaya and Sakai [10] reported that gypsum was also depleted in deuterium compared with the mother liquor. Whereas, for the ice-water [18], mirabilite ($Na_2SO_4 \cdot 10H_2O$)-water [19], and natron ($Na_2CO_3 \cdot 10H_2O$)-water [20] systems, D/H ratios are higher in the solid phase than in the mother liquor.

The δD value for the bulk water of crystallization of $NiSO_4 \cdot 7H_2O$ synthesized at 25° is -3.0 + 1.0%$_o$. This means that the D/H ratio of the bulk water of crystallization is lower than that of the mother liquor by 3.0%$_o$. The δD values of the bulk water of crystallization for $CuSO_4 \cdot 5H_2O$ and borax are -21.1 and 5.3% respectively at 25° [13,21].

The fractionation factor, α, between the bulk water of crystallization and the mother liquor is defined as

$$\alpha = (D/H)_{\text{bulk water of crystallization}}/(D/H)_{\text{mother liquor}}$$

The value of α obtained in this study at 25° is 0.997 ±0.001.

Result of fractional dehyderation at 0°. The relationship between the fraction of water dehyderated and duration time

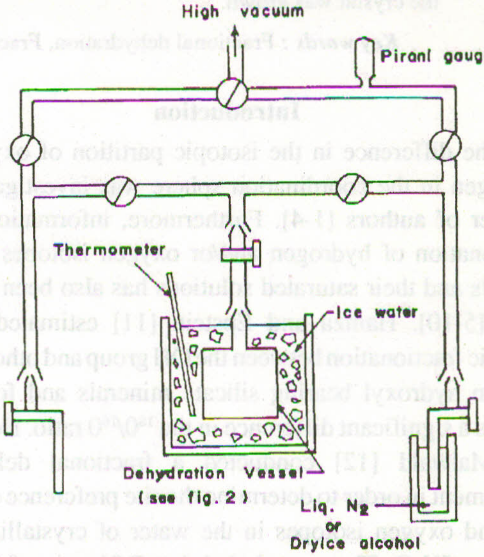

Fig. 1. System used for the fractional dehydration of $NiSO_4 \cdot 7H_2O$.

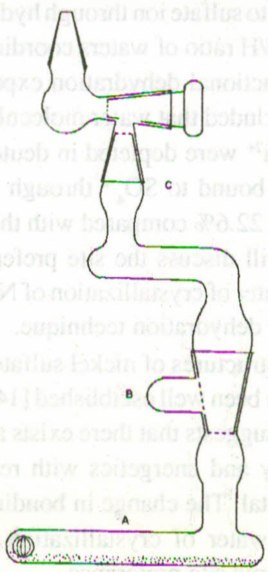

Fig. 2. Dehydration vessel used for fractional dehydration.

of dehydration is shown in Fig. 3. Here, F stands for the fraction obtained from the ratio of the quantity of water dehyderated to the total quantity of the water of crystallization initially present. Three straight lines drawn in the ranges. $0.045<F<0.268$, $0.268<F<0.480$, and $0.480<F$ reveal that the dehydration of water from the crystal may be regarded as three zeroth-order rate processes with different rate constants.

The relationship between δD of the water of each fraction and F is shown in Fig. 4. At F=0.045, a sharp maximum exists and there is a less conspicuous maximum at F=0.267.

The above result suggests that dehydration takes place not only from the surface of the crystal but also from the interior of the crystal randomly. If dehydration would take place layerwise from the surface of the crystal, δD of the water dehydrated should have remained constant, because δD was expected to be uniform in the crystal as δD of the mother liquor was practically constant during the process of crystal growth. In our study, since the dehydration process takes place randomly by a unique mechanism, it can be regarded as a "Rayleigh process".

Mechanism of dehydration. The structure of the tetrahydrate (IV) is assumed to be the same as that of site A of hexahydrate (VI) except that the two SO_4 occupy the opposite corners of the octahedron replacing two waters (Fig. 5).

Dehydration patterns shown in Fig. 3 and Fig. 4 may be explained as follows:

(i). One water molecule in site B of VII is dehydrated first since this water molecule is loosely bound in the crystal. The rate constant of dehydration of VII [22] is denoted by k_B (Fig. 5).

(ii). The facts that the change in dehydration rate takes place not at F=0.142 (corresponding to the quantity of one of seven water molecules) but at F=0.268 and that the maximum of δD exists in the range $0<F<0.268$, indicate that dehydration of VI also takes place before dehydration of site B water is completed. In other words, delayed dehydration of two water molecules from site A occurs with the dehydration of one water molecule from site B. The rate constant of dehydration of VI is denoted by k_A (Fig. 5).

(iii). As seen in Fig. 3, another straight line can be drawn in the range $0.268<F<0.480$. This indicates that site B water is completely dehydrated at F=0.268, and dehydration from site A and IV takes placed in the range $0.268<F<0.480$. If the intermediate phases, pentahydrate and trihydrate would exist in the process of dehydration, not two but three changes in the dehydration rate should have been observed in the range $0<F<0.710$. Therefore, we assume that two waters are dehydrated simultaneously during the change from VI to IV to II or the residence time of pentahydrate or trihydrate is quite short under the experimental conditions. The rate constant of dehydration from IV is expressed by k'_A (Fig. 6).

(iv). In the range $0.480<F<0.618$, we assume that the dehydration takes place exclusively from VI to give directly II, taking the fact that IV is not stable [23] into consideration.

(v) From the fact that F approaches 0.710 gradually beyond F=0.618 and never exceeds 0.710, II may not be dehydrated at 0°, *viz.*, II is inert for dehydration under the dehydration condition applied in this study.

(vi). Dehydration from all the species existing in the process of dehydration may be considered to have taken place

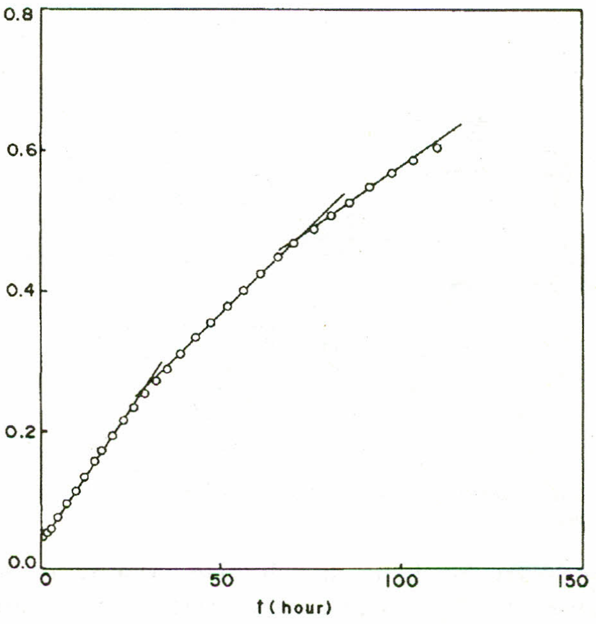

Fig. 3. Relationship between the fraction of water dehydrated (F) and duration time (t) of dehydration at 0°.

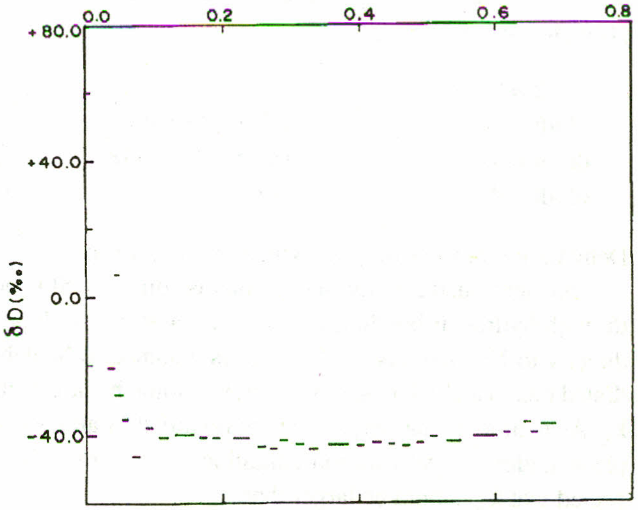

Fig. 4. Relationship between δD of the fraction of water dehydrated and the fraction (F) at 0°.

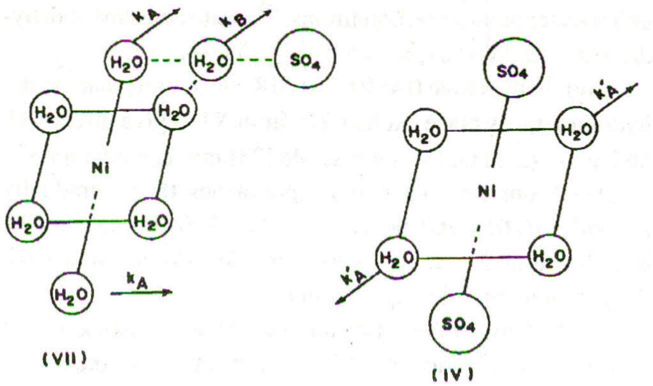

Fig. 5. Structure of the species assumed to exist in the process of dehydration.

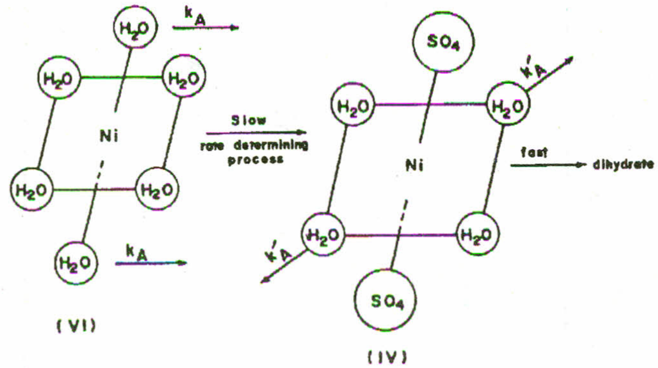

Fig. 6. Structure of the species assumed to exist in the process of dehydration.

by the zeroth-order reaction, because linerar relationships between F and time (t) exist as shown in Fig. 3. Simultaneous zeroth-order reactions give an overall zeroth-order reaction.

On the basis of the above facts and postulates, dehydration rate (dF/dt) at 0° in the range mentioned already may be presented as follows:

$$dF/dt = k_B + 2k_A \qquad (0.045 \leq F \leq 0.268) \ldots\ldots\ldots\ldots (1)$$
$$dF/dt = 2k_A + 2k'_A \qquad (0.268 \leq F \leq 0.480) \ldots\ldots\ldots\ldots (2)$$
$$dF/dt = 4k_A \qquad (0.480 \leq F \leq 0.618) \ldots\ldots\ldots\ldots (3)$$
$$dF/dt = 0 \qquad (0.710 < F) \ldots\ldots\ldots\ldots (4)$$

Dehydration process may be explained as follows:-

As mentioned already, site B water is bonded to SO_4^{-2} ion through hydrogen bonding and site A water is coordinated directly to Ni^{2+} ion. As site B water is assumed to be dehydrated more easily than site A water, k_B should be larger than k_A. As mentioned earlier, IV can be regarded as an unstable phase under our dehydration condition. Therefore, it is expected that k'_A should be larger than k_A

In the range, 0.480 < F <0.618, dehydration of IV depends on the dehydration of VI, since IV can not be dehydrated unless IV is generated by the dehydration of VI.

Accordingly, dehydration rate (k_A) of VI may be rate-determining and IV dehydrates immediately after dehydration of VI. Apparently, VI may directly change to II. Beyond F=0.480 the rate constant of dehydration should be equal to $4k_A$ and the rate equation in this range may be presented by Eq. (3), since the dehydration rate of VI is $2k_A$ and that of IV can be assigned to be $2k_A$. The process mentioned above is schematically shown in Fig. 6.

By measuring the slope of the straight lines in the ranges, 0.045<F<0.268, 0.268<F<0.480 and 0.480<F, it is possible to calculate k_B, k_A and k'_A by combining eq. (1), (2) and (3). The values of rate constants of dehydration at 0° together with ratios of rate constants of dehydration between different species are given below.

$$k_B = 5.87 \times 10^{-3}\ h^{-1}$$
$$k_A = 0.90 \times 10^{-3}\ h^{-1}$$
$$k'_A = 1.58 \times 10^{-3}\ h^{-1}$$
$$k_B/(k_B + 2k_A) = 0.766$$
$$k_A/(2k_A + 2k'_A) = 0.181$$

It is a known fact that lattice defects (lattice hole and dislocations) exist in the crystal and these are multiplied by cooling and pulverization [24,25]. Therefore, a network of dislocations is formed in the crystals of $NiSO_4 . 7H_2O$ used for fractional dehydration. If dehydration takes place mainly along dislocations, the dehydration in this system also can be regarded as taking place inside the crystal grains quite randomly.

Calculation of the site preference in the water of crystallization. Under the assumption that dehydration takes place randomly throughout crystal grains, a Rayleigh process can be applied for the analysis of fluctuations in the isotopic ratio of water collected fractionally [26]. The relationship between the change in isotopic ratio of dehydrated water and the fraction of water remaining is given in general by the equation

$$\delta D = \delta D^\circ + 10^3 r(1-\beta) \ln F_R \ldots\ldots\ldots\ldots (5)$$

where δD is the integral mean value of δD upto the i-th fraction, i.e. $\delta D = \Sigma F_i\ \delta D_i / \Sigma F_i$, δD° is the δD of the water of crystallization before dehydration, $r = F_R/(1-F_R)$, F_R is the fraction of remaining water in the crystal, and β is the kinetic fractionation factor of hydrogen isotopes for dehydration (and is equal to the ratio of the D/H for the dehydrated water to the D/H for the remaining water of crystal). Under the assumption that there is no exchange of water molecules between site A and B during dehydration at 0°, the Rayleigh process is applied to the curve (Fig. 3) in the range 0<F<0.045, where dehydration takes place exclusively from site B. The equation for the water dehydrated from site B of VII is presented in a similar fashion as eq. 5.

$$\delta D_B = \delta D_E^0 + 10^{10} r_B (1-\beta_B) \ln F_B \text{.................................} (6)$$

where subscript B stands for site B and F_B denotes the fraction of site B water remaining in the crystal.

By plotting δD_B versus $r_B \ln F_B$, δD_E^0 and β_B were calculated from the intersection with the δD_B axis and the slope of the line to be +98.1$\%_o$ and 0.861 respectively.

δD_A^0 the δD of the site A water before dehydration, can be calculated from the following relation among δD_A^0, δD_E^0 and δD (-3.0$\%_o$) of the bulk water of crystallization.

$$\delta D_E^0 + 6\ \delta D_A^0 = -3.0 \text{.................................} (7)$$

From equation (7), δD_A^0 was calculated to be -19.9% o. In the range 0.045<F<0.268, both sites B and A waters are dehydrated simultaneously. Therefore, the fluctuation of δD with respect to F should be represented by adding two Rayleigh equations for site B and A. The Rayleigh equation for site A is expressed in similar way as the equation for site B.

$$\delta D_A = \delta D_A^0 + 10^3 r_A (1-\beta_A) \ln F_A \text{.................................} (8)$$

where $r_A = F_A/(1-F_A)$ and subscript A indicates site A. In equation (8), the unknowns are δD_A, β_A and F_A. The relation between δD and the quantity of dehydrated water can be established by the following material balance equation:

$$M_B (1 + 10^{-3}\delta D_B) + M_A (1 + 10^{-3}\delta D_A) = M(1 + 10^{-3}\delta D) \text{..} (9)$$

where M represents the integral quantity of dehydrated water, δD is the integral mean δD value of dehydrated water, and M_A and M_B are the quantity of water dehydrated from site A and site B respectively.

The quantity of water dehydrated upto F=0.045 comes exclusively from site B, while the quantity of dehydrated water in the range 0.045<F<0.268 comes from both sites B and A which are 76.6% and 23.4% respectively, because $k_B/(k_B+2k_A)$ which is 0.766, is independent of the grain size as mentioned already. Since δD_E^0, δD_A^0 and β_B have already been calculated, β_A is the only unknown. Therefore, by combining eqs. 6 through 9, β_A can be calculated to be 0.976.

Conclusion

The results of this study indicate that the water of crystallization in the coordination sphere of the nickel ion is depleted in deuterium, while the water bonded to the sulfate ion through hydrogen bonding is enriched in deuterium as compared to the mother liquor.

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