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Proton Magnetic Resonance and the Hydrates of Sodium Halides

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Existence of the hydrates of the alkali halides is examined by a simple electrostatic model. The results explain the case of sodium halides fairly well.

The proton magnetic resonance spectrum of the hydrates of NaI, NaBr, and NaCl has been obtained. The spectrum of the powdered samples has the line shape characteristic of two-proton system. These hydrates are deliquescent and easily dehydrated, but there is no evidence of the motion of water molecules in the crystal up to the melting point. Water molecules in the sodium bromide dihydrate and the sodium chloride dihydrate have two orientations in the crystal.

§ 1. Introduction

Crystals containing water —hydrates— have been known widely. Many inorganic compounds are normally obtained as hydrates. There seems to be no simple ways, however, to determine whether a compound has its hydrate. The structure of the anhydrous material usually bears no simple relation to that of the hydrate.

On the other hand, PAKE[1] was the first to study proton positions of the water molecules in the hydrated crystal by means of the nuclear magnetic resonance (NMR) technique. Many papers on the NMR study of the hydrate have been reported since then. Recently YANO[2] reported that water molecules of the certain hydrates have the rotational states below melting point.

A hydrate of the alkali halide is one of the most simple examples to study the formation of the hydrated crystal. As for the sodium halides, there exist the hydrates of sodium iodide, bromide, and chloride, but no hydrate of sodium fluoride. All hydrated sodium halides are deliquescent and are easily dehydrated by desiccating agents such as calcium chloride. The binding of the water molecule in those crystals may be rather weak. There is likely to exist some kind of molecular motion of the water in the crystal even below melting point. Less symmetrical binding of the water molecule with its surroundings in the crystal, e.g. the hydrogen bonding, should prevent the molecule from this tendency. The structures of the hydrated sodium halides were investigated by WOOSTER.[3] The crystal structure of $NaCl \cdot 2H_2O$ and the detailed structures

of others, however, have been unknown.

In the present paper, first a brief account of the relation between the alkali halide and its hydrate is presented, using a simple electrostatic model. Next the experimental results of the proton resonence of the single crystals of $NaBr \cdot 2H_2O$ and $NaCl \cdot 2H_2O$, and of the powdered sodium halides are reported.

§ 2. Hydrates of Alkali Halides

The alkali halide M·X is one of the simplest compounds. To examine whether or not M·X has its hydrate $M(OH_2)X$, the electrostatic energies of both materials were compared. Since the water molecule has an electric dipole moment μ of 1.87 Debye,[4] it is rather hard to give an exact model for the calculation. If the point charge and the point dipole moment are assumed for the ion and the water molecule respectively, the energy difference ΔE [= electrostatic energy of $(M^+ \cdot X^-)$— electrostatic energy of $(M^+ \cdot OH_2 \cdot X^-)$] is written as follows:

$$\Delta E = \frac{e^2}{r_M + r_X} - \left\{ \frac{e^2}{r_M + 2r_W + r_X} + \frac{e\mu}{(r_M + r_W)^2} + \frac{e\mu}{(r_X + r_W)^2} \right\},$$

where e is the electronic charge, r_M and r_X are the ionic radii of M and X, and the effective radius of the water molecule r_W was assumed here to be equal to O–H distance in water vapor.[5]

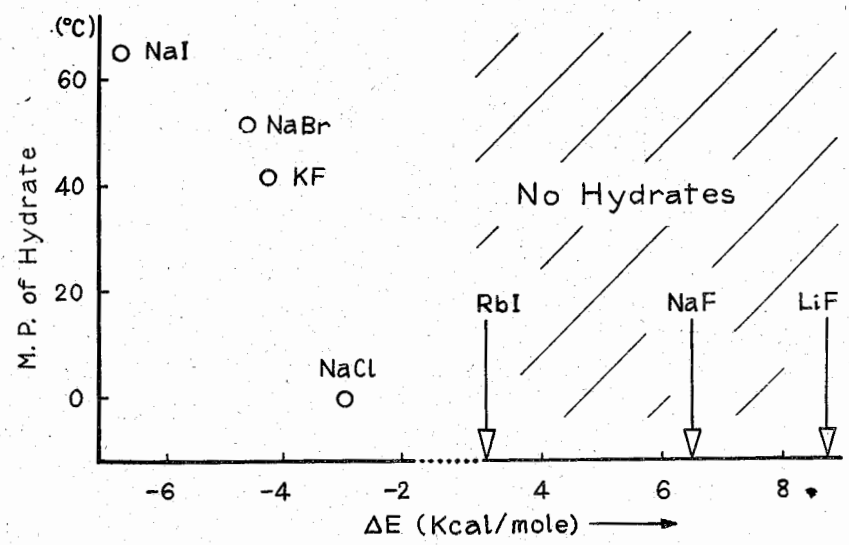

Fig. 1. Electrostatic energy difference ΔE between (M·X) and $(M \cdot OH_2 \cdot X)$ *versus* melting point of the actual hydrate. ΔE of the alkali halide which has no hydrate is represented by the arrow.

Calculated values of ΔE for sodium halides and some other alkali halides are shown in Fig. 1 with the melting point of their hydrate. The model used above seems to be too simple to represent the actual situation in the crystal. In fact, the hydrated alkali halides stated above are not monohydrates but dihydrates. Therefore, the numerical value of ΔE itself is not likely to have much significance. It is seen in Fig. 1, however, that there are hydrates of NaI, NaBr, and NaCl but no hydrate of NaF, and that the melting point of the hydrate goes higher as the absolute value of ΔE is greater. This suggests that the electrostatic interactions used in the above model should play the most essential part in the formation of the hydrate of ionic compounds.

§ 3. Experimental Procedure

Experiments were carried out using the NMR spectrometer. A block diagram of the apparatus is shown in Fig. 2. The electromagnet was excited by currents from 60 volts batteries. An autodyne detector was used as the radiofrequency oscillating detector. The measurements were undertaken with the following parameters: radio frequency = 18.5 Mc/s, applied magnetic field H = 4350 gauss, modulation amplitude = 1.0~2.0 gauss, and modulation frequency = 70c/s. A field uniformity of 10^{-4} over the sample volume was easily achieved.

Four 807 tubes were used as the magnetic field scanning apparatus, connected directly to the main magnet coil. About 5 minuts were needed to record

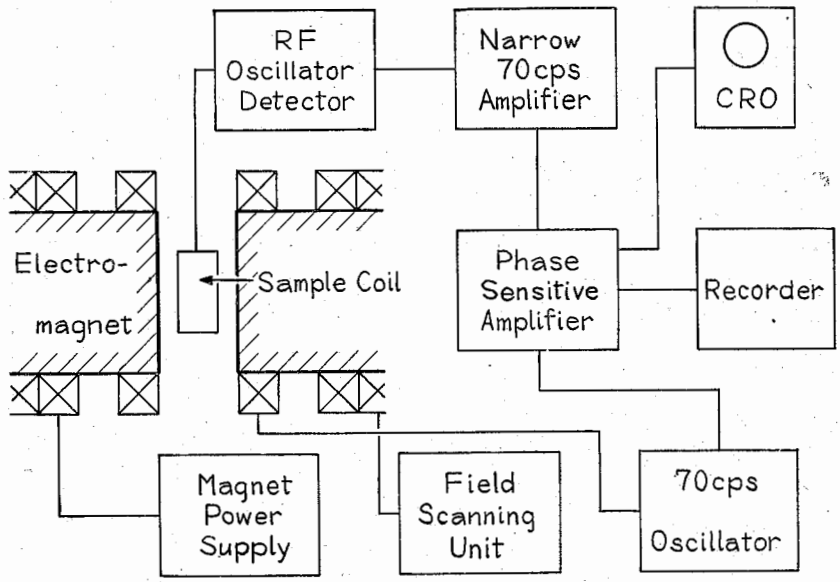

Fig. 2. Block diagram of the NMR spectrometer.

a whole resonance derivative. Most measurements were made above 0°C and a water circulated head was used so that the temperature of the sample was changed. Below 0°C, the head covered with porous polystyrene which contained dry ice was used and some adjustment was made to keep the sample at about −20°C for half an hour. In addition, a small dewar vessel was needed for measurements above liquid nitrogen temperature. Temperatures were measured by a copper-constantan thermocouple attached to the glass wall in the sample coil.

All crystals of the hydrated alkali halides were grown by slow cooling method from aqueous solution which was made with the powdered alkali halide of the best grade. The polycrystals of $NaI \cdot 2H_2O$ and $NaBr \cdot 2H_2O$ were obtained above room temperature. The cold chamber whose temperature was kept at about −20°C was used for preparation of poly- and single crystals of $NaCl \cdot 2H_2O$. The thin single crystals of the dihydrates of sodium bromide and sodium chloride were obtained and were made use of to measure the dependence of the proton resonance line on the angle between the applied magnetic field and an axis of the crystal.

§ 4. Results and Discussion

The angular dependence of the proton resonance line in $NaBr \cdot 2H_2O$ and $NaCl \cdot 2H_2O$ was obtained at room temperature and −20°C respectively. The structure of $NaBr \cdot 2H_2O$ is monoclinic and the unit cell contains four molecules, but positions of the constituent atoms have not been given.[3] Representative derivatives of the resonance line of $NaBr \cdot 2H_2O$ for various directions of the external

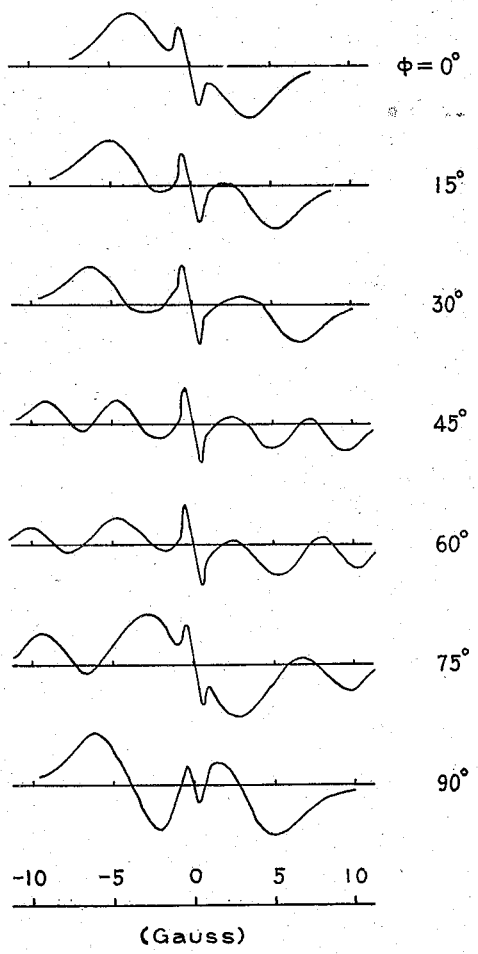

Fig. 3. The dependence of the proton resonance line derivatives of $NaBr \cdot 2HO_2$ on the angle ϕ between b-axis and the applied magnetic field H_0 in a-b plane.

magnetic field H_0 in a-b plane are shown in Fig. 3. It is shown in the figure that the spectrum has a fine structure, and is similar to that of gypsum[1] except the center peaks due to the adhering water.

If proton pairs of the water molecules in the crystal exhibit only dipole-dipole interaction, the line pair separation δH in the fine structure of Fig. 3 is given by the formula

$$\delta H = 2\alpha \left\{ 3\cos^2(\phi+\phi_0)\cos^2\delta - 1 \right\},$$

where $2\alpha = 3\mu_p/r^3$ in which μ_p is the proton magnetic moment and r is the inter-proton distance. And 2α was 10.5 gauss. Angles ϕ, ϕ_0, δ are shown in Fig. 4(a). Experimental values of the line pair separation and the calculated ones in which ϕ_0 and δ are taken as $\pm 52°$ and $\pm 20.5°$ respectively, are plotted against the angle ϕ in Fig. 4(b). This figure shows that there are two directions of the proton-proton line in the crystal. The two proton-proton lines of different directions are possibly the reflection in the a-c plane of each other. Unfortunately, analysis can not be pushed further because, as stated above, the exact positions of the constituent atoms are unknown.

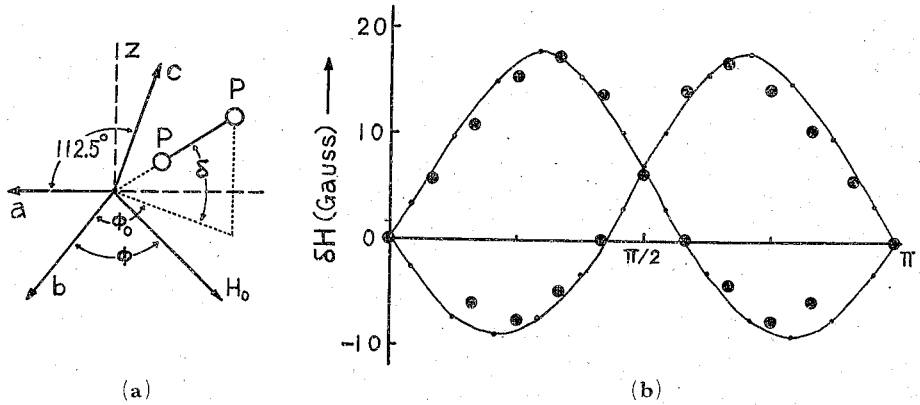

Fig. 4. (a) Diagram of the relations of the applied field H_0 and the proton-proton line to crystal axes of the sodium bromide dihydrate.
(b) PAKE curves for $NaBr{\cdot}H_2O$ rotated about the z-axis. Solid curves are the plots of the theoretical value for $\phi_0 = \pm 52°$, $\delta = \pm 20.5°$, and $2\alpha = 10.5$ gauss.

$NaCl{\cdot}2H_2O$ has not been studied by X-ray method as it decomposes rapidly at ordinary temperatures. Its crystal figure and habits are very similar to those of $NaBr{\cdot}2H_2O$. Actually, the crystal cut to have the same figure as $NaBr{\cdot}2H_2O$ showed almost equal patterns of the angular dependence of the proton resonance spectrum. Therefore, the water molecules in $NaCl{\cdot}2H_2O$ have also two orien-

tations of the proton-proton line. The signals of this crystal, however, have very low signal-to-noise ratio due to the saturation effect of the *r-f* field and to the small volume of its crystal.

The proton resonance lines of the hydrates of NaI, NaBr, and NaCl in powdered state showed the line shape characteristic of the two-proton system. Their second moments had the values of 22~25 gauss[2] far below the melting point and apparently became smaller as temperature rose near their melting point. The small second moments are mostly due to the central peaks caused by the water occluded in and/or adhering on the powder. As an example, the temperature dependence of the resonance line of NaI $2H_2O$ is represented in Fig. 5. The powdered crystals of NaI·$2H_2O$ and NaBr·$2H_2O$ melted at several degrees below their melting point described in the text-books. Fig. 5

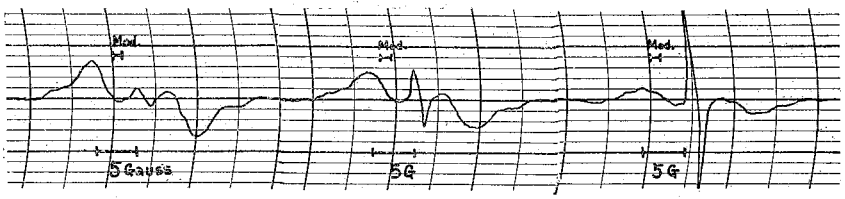

Fig. 5. The proton resonance line derivatives of the sodium iodide dihydrate at 20°, 50°, and 60°C.

shows that there is no radical change in the line shape, differing from the case of the certain hydrates whose water molecules are in rotational state below the melting point.[2]

It should be concluded that the water molecules in the hydrated sodium halides have no motional state below the melting point, though some kind of motion is expected from their deliquescence and easy dehydration. The hydrogen bond concept has been applied to the hydrates containing halogen atoms.[2),6)] This bond may hinder the molecular motion of the water molecule in the crystal. It should be noticeable, however, that the molecular motions of the water are prevented even in the case of sodium iodide dihydrate despite the small electronegativity of iodine ion and the rather high melting point of this crystal.

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