Proton Conductivity in Lithium Sulfate Monohydrate and the Motion of its Water Molecule

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Proton conductivity is established in lithium sulfate mono-hydrate by electrolysis experiments in the solid state. This effect is discussed in relation to the large amplitude oscillations of the water molecule as evidenced by proton magnetic resonance measurements at different temperatures. The importance of unidirectional chain-like structure of hydrogen bonds in this substance is emphasized, and several implications of the proton conductivity are mentioned.

INTRODUCTION

Lithium sulfate monohydrate seems to be a peculiar substance whose studying so far by various techniques resulted in almost as many different views as there are authors. The basic question concerns the position of the hydrogen atoms and little further success may be expected before neutron diffraction studies are made.* However, there is definite evidence of a specific motion of the water molecule from quadrupole perturbed magnetic resonance spectra of the deuterated compound[1]. McGrath et al.[2] have also observed a change with temperature in the line separation of proton magnetic resonance spectra at definite orientation of a single crystal.

It occured to us that the motion of the water molecule in this compound may have some relation to proton migration. This seemed likely according to the proposed hydrogen bond arrangement[3] and the anisotropy of electrical conductivity[4]. Probably because of the apparent simplicity of this compound most of the proton magnetic resonance work has been done on single crystals and there is only one brief information on powder spectra[5]. We therefore started a combined research of the temperature dependence of p.m.r. powder spectra together with experiments required to test the postulated proton migration in this compound.

EXPERIMENTAL

I. *Samples*

a) Preparation. — In the first experiments an analytical reagent (»Erba« - product) was used. This was later recrystallized because fine powder was needed for the electrolysis experiments. For this purpose a saturated solution was prepared at room temperature and then quickly transferred under rapid stirring into water at 80⁰C. Due to the negative temperature coefficient of solubility finely crystallized powder precipitated. After drying on a filter paper it was left at room temperature

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in a closed vessel without any drying agent, the composition being checked at intervals by determining the loss on dehydration.

b) Analysis. — Lithium sulfate monohydrate looses its crystal water above 100^0C[6]. The completness of the dehydration was checked up to 150^0C. In all the determinations the total loss on dehydration was found to be close to the theoretical value of $14.08^0/o$. The maximum surplus of water for the recrystallized sample was $1.14^0/o$ of the theoretical amount. The SO_4^{2-} content was also checked by Ba-sulfate precipitation, and the obtained result was equivalent to $2.3^0/o$ deficiency in water.

II. *Proton magnetic resonance measurements*

The apparatus was of the conventional bridge-type[7,8]. The temperature-stabilized crystal oscillator of 29.000 Mc/s had a long term stability of about 1 part in 10^5. The twin-T-bridge was carefully insulated both thermally and electrically and connected directly to a commercial radio receiver with a maximum band width of 5 Kc/s. The output of the phase sensitive detector was fed into a mA-meter recorder. The slow sweep drive for the magnetic field was synchronised from the recorder motor. The electronically stabilized[7] current of about 1.5 A for the electromagnet showed over 30 minutes a stability of 1 part in 10^5.

The pole faces of the magnet had a diameter of 15 cm and were finely ground. The assembled magnet had a nonparallelism of the pole faces of 0.03 mm as measured with calibrated hard-steel edges, and the homogeneity of the magnetic field over the sample is estimated to be better than 0.2 gauss.

The slow sweep calibration was done by using beats between the crystal oscillator and a Marconi variable frequency generator with a suitable mixer feeding into a frequency counter[9]. The curvature of the »reversible« hysteresis loop at 6811 gauss was found to be negligible and the slow sweep change of the field with time linear for the present purpose.

The working temperature of the magnet in its 33 mm gap is about 40^0C. For temperatures from about 15^0C to 150^0C a circulating system with a constant temperature bath was used. The two lower temperatures in the present work were attained by immersing the probe into a Dewar vessel filled with either liquid nitrogen, or with dry ice-acetone mixture. In all the measurements the probe was air-tight.

III. *Electrolysis experiments*

The electrolysis cell consists of two symmetrical parts (one half is shown in Fig. 1), the joining faces of which are ground glass flanges. The main body of the cell is jacketed, thus, the material under test and the mercury electrodes can be thermostated at will. A capillary is used to measure the volume of evolved gas which causes the displacement of mercury. It is bent to a knee of 2 cm height to ensure a constant gas pressure. The capillary is made of precision bore tubing of 1.00 mm
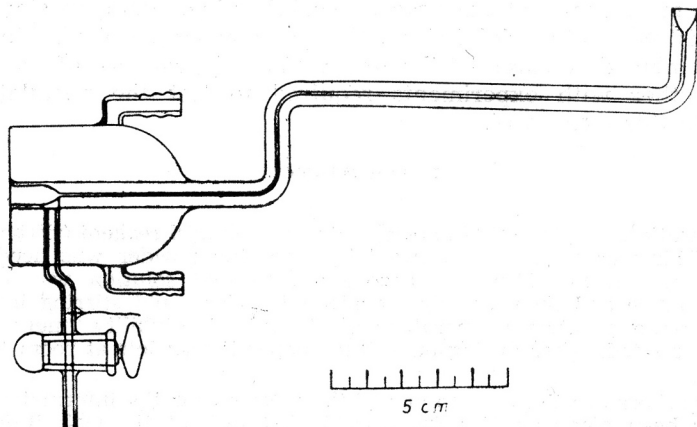

5 cm

Fig. 1. The electrolysis cell; one of the two symmetrical parts shown.

inner diameter. The displacement of the meniscus was followed by a cathetometer (for slow rates), or by taking readings from an attached mm scale. The contacts to mercury were small pieces of platinum wire fused in glass.

The solid material to be tested was pressed into pellets of 13 mm dia. in a hydraulic press. Pressures up to 300 kg/cm² were used. Often, the obtained pellet showed surface cracks and had to be discarded. In fact, it was almost impossible to prepare pellets from mechanically pulverized material. Better results were obtained with the recrystallized lithium sulfate (see sec. I). The pellet had to withstand certain stress when mounted into the cell. In order to prevent any leakage of gas it was fixed by polyester resin cement (»Araldite«) to the ground glass-flanges. Besides low strength the bare lithium sulfate pellets showed poor quality contacts with mercury. In addition, gas evolution caused appreciable displacement of mercury diminishing the contact area between mercury and the pellet. This resulted in a maximum in the current *vs.* time plot after which the process came to a standstill. To avoid this, »sandwich« pellets were tried. To both sides of a lithium sulfate pellet graphite layers were pressed. Each side had 7.5% graphite of the lithium sulfate amount — 0.583 g. — which always resulted in equal pellet thicknesses. Bright, strong, and well defined surfaces were obtained. With such pellets no maximum in the current — time plots at constant field was found. The only other difference with respect to the experiments with »bare« pellets was a time lag in the mercury displacement after the circuit was switched on. This has been ascribed to the diffusion of gas through the graphite layer.

The electrolysis was performed using regulated, stabilized high voltage supply units, several in series if high fields were necessary. The current was measured by a light-spot microammeter up to 750 microamps. For higher values it was replaced by a pointer mA-meter. The voltage was measured by a precision voltmeter. All the wires were insulated and suspended in air by pieces of insulating tape. The outer surfaces of the glass cell were carefully cleaned. In all the experiments the cathode side of the cell was earthed. In spite of all these precautions there were small leakage currents which were corrected by instrument scale zero correction.

It is impossible in case of crystalline hydrates to apply any technique operating in vacuum[10] because of the dehydration. The evolved gas was therefore identified as hydrogen by introducing it into a solution of palladium chloride. A thick, black, deposit formed after a few hours, while the blank solution exposed to air remained unchanged. The colloidal precipitate was proved to be elementary palladium.

RESULTS

To obtain reliable values of second moments at various temperatures a modulation amplitude of 3.6 gauss had to be used. This is accounted for in the usual way in the final results[11]. The time constant of the recording system was only 3 sec. and the corresponding second moment correction was therefore negligible[12]. Each half of a curve was treated separately. The difference between the means of the two halves was in general less than 1 gauss². The standard deviations given in Table I are calculated for the total mean value.

Even with the 3.6 gauss modulation amplitude the observed spectra show definite change in their shape with temperature. Only at —196°C was the modulation amplitude 4.5 gauss. In Fig. 2. are shown the spectra obtained only at the three higher temperatures at a sufficiently low RF-level to avoid saturation distortions.

We experienced considerable difficulty in obtaining symmetrical line shapes owing to different saturation behaviour of their narrow and broad components. This is illustrated in Fig. 3. where the true line shapes (modul. ampl. 1.2 gauss) are reproduced. It is not a progressive saturation experiment but merely a check on the line shapes at different RF levels.

An electrolysis experiment of a sandwich pellet is shown in Fig. 4. It took about half an hour at 100 V to attain the same current as before an interruption

of 19 hours. During this period the whole assembley was thermostated, and only the circuit was switched off. The mercury displacement, which took place on the cathodic side was followed in the beginning of the experiment as seen in Fig. 4. Later, we emptied the whole capillary in such a way as to preserve
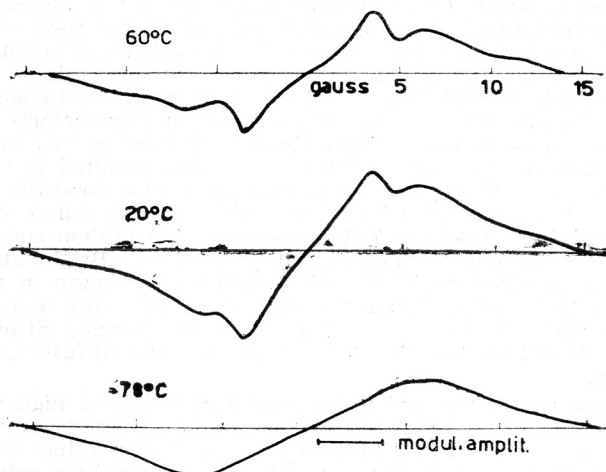

Fig. 2. The proton magnetic resonance curves of $Li_2SO_4 . H_2O$ at different temperatures.

sufficient electrical contact while at the same time leaving free escape of gas through the capillary.

After this experiment the pellet was carefully freed of graphite and divided into the anodic and cathodic portions. From both of these and from an original sample of $Li_2SO_4 \cdot H_2O$ X-ray powder photographs were taken, but no change in the crystal structure was observed.
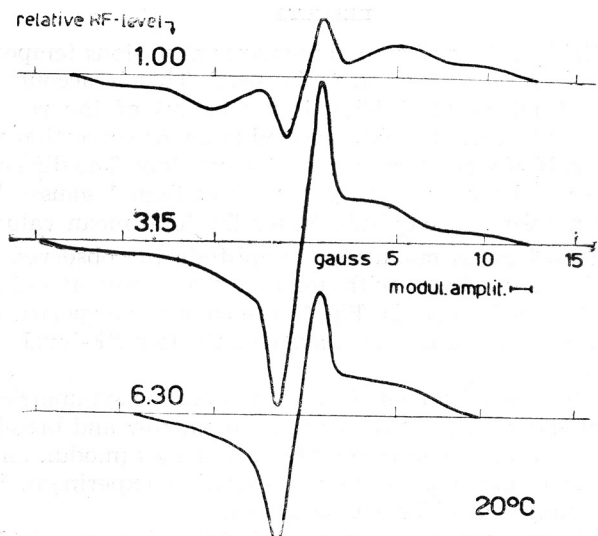

Fig. 3. The proton magnetic resonance curves of Li_2SO_4 H_2O at 20⁰C for different RF-levels.
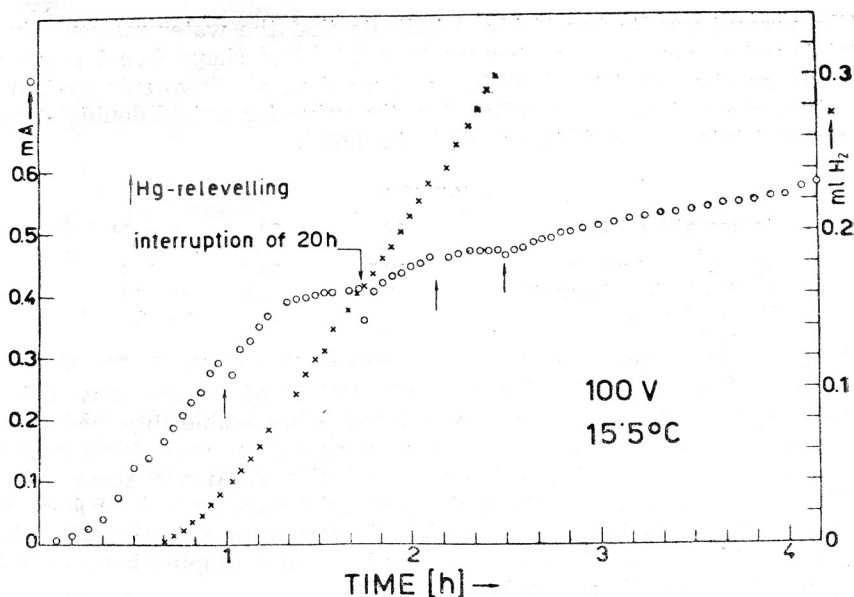
Fig. 4. The kinetics of hydrogen evolution during electrolysis of $Li_2SO_4 \cdot H_2O$ pellet at 100 Volt and 15.5°C

DISCUSSION

From the numerical values quoted in the only available powder work on $Li_2SO_4 \cdot H_2O$[5] one calculates a second moment of 28.2 gauss² at room temperature. Its relative error is 25%, and no line shape is reproduced. Our value (see Table I) is 19.7 gauss² with a 5% relative standard deviation. The present value obtained even at liquid nitrogen temperature is smaller than the discussed room temperature second moment of 28.2 gauss². We therefore take 25.5 gauss² as the second moment of a »rigid and stationary« water molecule in this compound. McGrath et al.[2] quote an orientation independent 2 gauss line width of their single crystal proton resonance peaks. This corresponds to approximately 1 gauss² for the intermolecular broadening. The intramolecular second moment is therefore taken as 24.5 gauss², and from this the interproton distance in the water molecule,

$$r = (358.08/24.5)^{1/6} = 1.57 \pm 0.02 \text{ Å},$$

without zero-point vibrational correction. The standard deviation includes only the error of the second moment measurements, but not the uncertainty in estimating the intermolecular contribution. This is not likely to add more than ± 0.01 Å. The same value for the interproton distance was obtained by Soutif and Ayant[5b] from single crystal measurements, but at room temperature. Hirahara and Murakami[13] give for their single crystal measurements (also at room temperature) 1.59 Å. McGrath et al.[2] give no explicit value for this interproton distance because of the »Pake shifts« in their single crystal measurements, an effect fully explored by them and not discussed by the former authors.

The present results (see Table I) indicate that the water molecule in this crystal is not at rest at room temperature. The line shape (see top curve in Fig. 3) shows characteristic shoulders and maxima of a two spin system, but with a line width about 30% smaller than the value for a rigid doublet. At 60°C the apparent interproton distance would be 1.66 Å.

TABLE I

temperature [°C]	60	20	—79	—196
sec. mom. [gauss²]	18.5	19.7	23.1	25.5
± stand. dev. [gauss²]	0.9	1.1	0.4	2.0
No. of measur.	6	6	8	10

McGrath et al.[2] found evidence for some motion of the H_2O molecule by making spot checks at 77°K for a few orientations of a single crystal in the magnetic field. On the other hand they found it impossible to explain all the puzzling features of the single crystal p. m. r. spectra at room temperature by taking into account several posisble motional effects. Among these only the 180° flip-flop reorientation of the water molecule[1] appears to have been established experimentally in $Li_2SO_4 \cdot D_2O$, but the spectrum of $Li_2SO_4 \cdot H_2O$ shown in Fig. 3 (top line) cannot be accounted for by such a flipping because it does not change the magnetic spin-spin coupling[2,14].

As the central peak becomes important we shall discuss its origin in more detail.

Hirahara and Murakami[13] noted a sharp peak in their measurements too. They attributed it to the presence of free water in the cracks of the sample, and found it to disappear on dessication. McGrath et al.[2] reported that very small amount of free water in the lithium sulfate crystals produced a small narrow signal at room temperature, but do not specify any analytical data. It is not described in ref. 2 how the crystals were grown, while in ref. 13 they were grown at 80°C. There is evidence[15] that at this temperature nearly perfect crystals should be obtained in contrast to growing them at 20°C or 40°C.

To measure the proportion of protons causing the narrow component one has first to separate it from the total curve. For the sake of simplicity we adopt the following procedure which is sufficiently accurate for the present purpose. The rigid water maximum slope line width is taken as 13.5 gauss, and the separation at the points where such a line crosses the abscissa and that at the negative minima are taken as 5.7 and 2.8 gauss resp. Our curve (top Fig. 3) is a mean shape visually estimated through 6 superimposed experimental lines. Using its maximum slope line width and the given values for a »rigid« line one can roughly reconstruct the middle portion of the experimental doublet mean curve. The first moments were calculated for each half and the percentage of protons belonging to the narrow part found to be 9.7 and 9.2.

In none of our experiments have we been led to ascribe more than 0.20% of the substance to admixed water (and in several cases there was a certain deficiency of water). The above line shape analysis requires seven times as much free water. This suggests that the narrow component of the proton magnetic resonance spectra in lithium sulfate monohydrate at room temperature is due to protons which are an integral part of the crystal water framework in this substance. McGrath et al.[2] consider that the central peak at 77°K is a curve of half width 2 to 3 gauss due to frozen water. This is difficult to reconcile with the ice p. m. r. line width of 16.2 gauss below 200°K.[16]

Results shown in Fig. 3 indicate that the two regions of the proton resonance absorption have different relaxation mechanisms. Although this would be consistent with any kind of admixed water it is also consistent with rather freely moving part of protons. According to our results the central portion has very low intensity at about 200°K, while the second moment has significantly increased as compared with its value above room temperature. The Raman spectra[17] at 153°K give different results from those obtained at room temperature[18], which is interpreted by the presence of two different orientations of the water molecule[17]. All this evidence is supporting the view that the water molecule in lithium sulfate monohydrate is undergoing a certain change between 150° and 300°K. Its free rotation can definitely be rejected because the reduction factor of the second moment (from — 196 to 60°C) is 0.725 and not 0.25 as in the case of a water molecule rotating around the bisectrix of the H-O-H angle.

In borax, $Na_2[B_4O_5(OH)_4] \cdot 8 H_2O$, free rotation of water molecules was also found to be inconsistent with the p. m. r. results[19], but it was impossible to ascribe a definite kind of motion owing to the complicated structure. In the present case there is one molecule of water per formula unit, and it is only the question of the orientation of the axis of hindered oscillations that cannot be answered. If this axis is normal to the interproton vector the second moment reduction factor yields an angular amplitude of oscillation of about 25°. If it is along a hydrogen bond the amplitude rises to about 50°[20]. Both values are very large and it would be interesting to see what would yield the neutron diffraction.

Borax, in which the water molecules are possibly also subject to similar large amplitude hindered oscillations[19], shows protonic conductivity[21], so that one might suppose that such a mechanism in lithium sulfate may be related to the p. m. r. results.

If we accept Larson and Helmholz's crystal structure[3] as basically correct (but see for comment ref. 22, footnote 12) then the hydrogen bond arrangement along the b-axis seems very favourable for the migration of protons. The actual mechanism is far from being clear, but in addition to some kind of reorientation of water molecules, there should be a net translation of protons along the hydrogen bond chain. The hydrogen atom in the shortest 0—0 bond (2.87 Å) is facing an oxygen from the sulfate group. Although this hydrogen may take part in some kind of reorientation this direction is a dead end for an effective migration of protons. On the contrary, the continuous zig-zag line connecting water oxygens along the b-axis is almost like a tube through which effective migration of protons can take place. This is in agreement with the electrical conductivity measurements[4] showing largest specific conductivity along this direction. It has also a positive temperature gradient characteristic of semiconductors, a fact established in borax[21] too.

In our lithium sulfate electrolysis experiments the Faraday law was fulfilled by about 30% when a bare pellet was used in contact with mercury. In the first experiment with the sandwich pellet the evolved gas corresponded to 63% Faraday efficiency to increase to about 100% in the experiment shown in Fig. 4. This, together with the proof that the evolved gas was hydrogen, is a definite evidence that the current in lithium sulfate monohydrate is dominantly carried by protons. It is noteworthy that in $Li_2SO_4 \cdot H_2O$ this mechanism

is very effective even at 15⁰C as different from borax[21]. The later exhibits a kink in its log-conductivity *vs.* 1/T curve while in the same temperature range there is only one straight line for lithium sulfate. It would be interesting to search for such an effect in it at lower temperatures.

The main purpose of this electrochemical part of the present inevstigation was to find out whether there is protonic conductivity in lithium sulfate. Fig. 4. is reproduced as an illustration of the general features of the kinetics of this process. However, the established protonic conductivity has several implications.

First, it requires some motion of water molecules, or, more generally, of their protons. The presented p. m. r. results are in agreement with this. On the other hand, if the narrow component of these spectra is ascribed to »free« protons, then their concentration (about 10⁰/₀ of all protons) is by far too large as compared with proton dissociation in ice[23], which is regarded as a model substance for proton conductivity. Thus, a direct relation between the shape of the p. m. r. spectra and proton migration is not evident. Experiments at closely spaced temperatures, as in the case of borax[19], and a clear picture of the proton migration mechanism is needed before one could estimate its importance for the proton magnetic resonance experiments. At present it seems that the described results further complicate the already difficult problem of proton magnetic resonance in lithium sulfate monohydrate, because large amplitude hindered oscillations of the water molecule at room temperature cannot be neglected.

Second, this substance may prove to be at least as interesting in studying proton conductivity as ice. It has only one molecule of water per formula unit. The water molecules appear to be arranged in the crystal lattice in isolated »unidimensional« chains. They run along the b axis, which is also the pyro-electric axis. It would not be surprising if the unaccounted pyroelectric effect (70⁰/₀ of the total one) in this subtsance[24] is due to proton migration. For instance, by setting up a temperature gradient across an ice crystal Latham and Mason [25] were able to measure its thermoelectric force caused by sub-stantially greater mobility of protons than hydroxyls.

The proton conductivity has so far been directly established in two cases: in cetyl alcohol[10] and in ice[26]. The term »protonic semiconductor« seems to have been invoked for the first time by N. Riehl[27] in case of ice and later independently used by Bradley[28] and discussed at length by Eigen and De Maeyer[23]. Both borax[21] and lithium sulfate monohydrate have positive temperature gradients of electrical conductivity. In the former compound the activation energy (ref. 21 unpubl. results) is comparable to that of ice, while the latter one has twice as large a value[4], but still within limits encountered in semiconductors. The example of cetyl alcohol and lithium sulfate monohydrate show that the presence of large proportion of water in the crystal lattice is not important. The more stringent condition for proton conductivity appears to be certain type of favourable hydrogen bond arrangement. Thus, protonic semiconductors should be expected among other inorganic and organic hydroxo hydrates.

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IZVOD

Protonska vodljivost u monohidratu litijeva sulfata i gibanje njegove molekule vode

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Elektrolizom u čvrstom stanju ustanovljena je protonska vodljivost u monohidratu litijeva sulfata. O toj se pojavi raspravlja u odnosu na velike amplitude oscilacija molekule vode, što proizlazi iz mjerenja protonske magnetske rezonancije kod različitih temperatura. Istaknuta je važnost usmjerenih lanaca vodikovih mostova u ovom spoju i spomenute su neke posljedice pojave protonske vodljivosti.

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