Journal of Advances and Scholarly Researches in Allied Education
Vol. 18, Issue No. 6, October-2021, ISSN 2230-7540

Studies Spectroscopic of Water Groups in Hydrates

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Abstract – An introduction to hydrated salts. Beginning with a brief historical introduction to blue vitroyl, the bonding of water groups in a hydrated salt has been explained here. The various modes of motion of water groups with regard to spectroscopic studies have also been described in this chapter. The importance of thermal deaquation and further of deaquation in electric field have been emphasized.

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INTRODUCTION:

The water molecules embedded in hydrated salts have aroused the interest of scientists since centuries.

This started with the determination of dehydration steps for many commercially useful hydrated compounds like blue vitroyl, green vitroyl, potash alum, gypsum, Mohr's salt etc.

Clathrates and Crystal Hydrates:

Cl athrates are basically cages of water molecules inside which molecules of some coordinating compound become trapped. They have not gathered much interest as their highly undefined coordination baffles the research for systematic about the dynamics of crystalline water [1].

Simple Heating of Salts:

Blue vitroyl ($CuSO_4.5H_2O$) was earlier known to lose four H_2O groups per molecule of hydrated compound at about 100°C and remaining last water molecule at a much higher temperature of about 230°C. Paulik [2] detected three distinctive deaquation steps of $CuSO_4.5H_2O$ viz., 2 moles, 2 moles and 1 mole of water, emphasizing that these separate steps could be distinguished only when using a polyplate holder. However Sarig [3] could detect three distinctive deaquation steps of $CuSO_4.5H_2O$ at temperatures of 85°C, 107°C and 231°C using a simple micro-crucible, the decomposition being carried out on a Mettler Thermoanalyzer in controlled dry nitrogen flow.

Bonding of H_2O Groups in a Salt:

The water molecules are supposed to be bound within a hydrated salt systematically. Even water molecules get bound in NaCl, when $NaCl.2H_2O$ [4] compound is formed.

The compounds in the series $MSO_4.H_2O$ [M=Mg, Ni, Cu, Co, Fe, Zn, Mn] all contain a strong bonded water molecule in their structure, accounting for their thermal stability. This was established by Oswald[5] through I.R. and NMR studies.

Oswald also concluded that the concept of structure like MH_2SO_5 or $M(OH)SO_4$ existing in $MSO_4.H_2O$ is wrong.

Free and Bound Water:

The internal binding within a water molecule is adequately represented in terms of sp^3 hybridized orbitals[6]. The two O—H bonds and the two lone pair orbitals on the oxygen atom, projecting above and below the molecular plane, make water molecules go favourably into tetrahedral coordination on entering into a condensed phase (Fig 1.1). H-atoms become involved in binding through hydrogen bonds (H bonds), and the oxygen atom (O_w) forms some coordination bonds or acts as an acceptor for other H atoms.

The Geometry of Water in Hydrates:

Since X-ray diffraction does not yield accurate measurements on the positions of H atom, neutron diffraction methods have been used to obtain the geometry of water molecules in hydrates. Table 1.1 gives the relevant data [7-14]. In general the O—H bond length $r(O_w—H)$ and the interbond angle (2α) become larger in the bound state as compared with free water.

The Hydrogen bonds are energetically intermediate between covalent and van der waal bonds and if stability conditions require, the H—bond angle (O_w—H……X) may deviate considerably from 180º, while the H—O—H angle of water deviates very little from that in free state [15].

Spectroscopic Studies of Water Groups in Hydrates:

Water, being a nonlinear triatomic molecule (symmetry C_{2v} in free state) has in all 09 modes of motion, of which 03 are internal (ν_1, ν_2 and ν_3), 03 rotations (R_x, R_y and R_z) and 03 translations (T_x, T_y and T_z). The dynamics of water in crystal hydrates can be described in terms of 03 internal modes and 06 external modes of water. The 06 external modems are specifically the 03 hindered rotations or liberational modes (LM_s] and 03 hindered translational modes (T_rM_s). The librations are also termed as wagging (W), twisting (T) and rocking (R) modes.

Importance of LMs:

Each crystallographic district set of water molecules gives its own set of LMs which provide the necessary information in terms of the frequencies, intensities and half widths, and the temperature dependence of all these, from which the nature of the acting crystalline field can be deduced [16-18]. The fact that the LMs are more sensitive than the internal modes to environmental changes makes the LMs useful to phase transition studies [19] as well. The multifold potential well for librations with finite barrier heights V_o makes the LMs useful for NMR[20] response as well.

Thermal Deaquation:

The hydrated salts loose water on heating. Such water molecules must be getting detached from their positions in the crystal lattice at some temperature. If the number of water groups per molecule of the salt is more than one, the different water groups participating in deaquation must be detached at different temperatures, as per their bonding in the lattice.

TG, DTG and DTA analyses provide sufficient information on thermal deaquation of hydrated salts. The corresponding graphs for $CuSO_4.5H_2O$ as obtained by Sarig [3] for the heating rate of 2°C/min. are quoted in Fig. 1.2. The thermogravimetric results of Sarig[3] for this salt and also for $NiSO_4.7H_2O$ can easily be explained by the different number of bonds and their different strengths that the water molecules have to break, in order to escape from their respected hydrated sulphates.

It has been established that all other conditions being equal, the slower the rate of heating, the better the separation of deaquation steps, Paulik [2] has established that water vapour diffusion equilibrium is established over the sample during heating. The controlled inert gas flow if employed prevents the establishment of such an equilibrium, thus facilitating the separation of deaquation steps.

Deaquation in Electric Field:

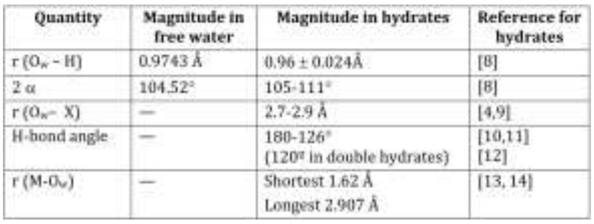
The electric field applied to the hydrated crystal during thermal deaquation ionizes the water groups into H^+ and OH^-. These ions are carried respectively to the cathode and anode respectively. This then leads to observation of peak in the electrical conductivity vs temperature plot.

Srivatsa and Pandey [21] have made electric field controlled deaquation studies in some hydrated salts containing six water groups per salt molecule. These authors have been able to identify peaks corresponding to differently attached water groups in some Tutton salts through above studies.

It would therefore be interesting to select some new hydrated systems for electric field controlled deaquation studies.

Table

Geometry of Water in Crystal Hydrates



Quantity	Magnitude in free water	Magnitude in hydrates	Reference for hydrates
r (O_w – H)	0.9743 Å	0.96 ± 0.024Å	[8]
2 α	104.52°	105-111°	[8]
r (O_w– X)	—	2.7-2.9 Å	[4,9]
H-bond angle	—	180-126° (120° in double hydrates)	[10,11] [12]
r (M-O_w)	—	Shortest 1.62 Å Longest 2.907 Å	[13, 14]

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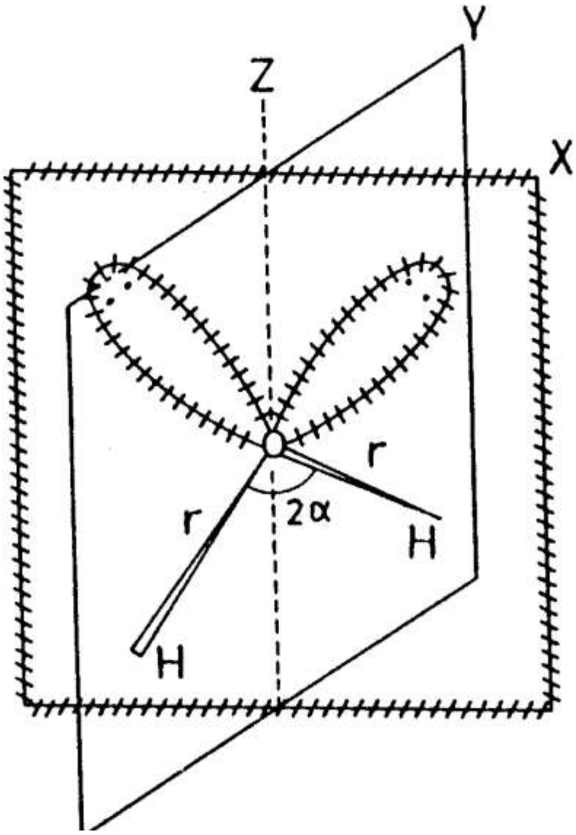

FIGURE 1.1: THE TETRAHEDRAL COORDINATING NATURE OF WATER MALECULE THE LONE PAIR ORBITALS ON OW ARE SHOWN IN ADDITION TO THE TWO O-H BONDS

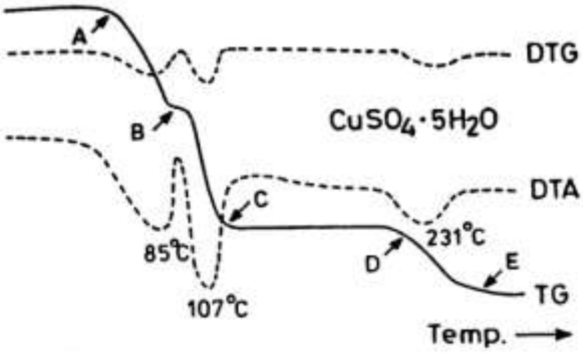

FIGURE 1.2: DEAQUATION OF CUPRIC SULFATE PENTAHYDRATE

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