Deaquation process in ammonium Tutton salts through electrical and dielectric measurements

K M K SRIVATSA and S D PANDEY*

Physics Department, P P N College, Kanpur 208 001, India

Abstract. The d.c. electrical conductivity (σ), dielectric constant (ε') and thermogravimetric analysis studies are reported in the temperature range 20–280°C for zinc ammonium sulphate hexahydrate and magnesium ammonium sulphate hexahydrate Tutton salts. The results are attributed to the release of water molecules at the respective dehydration temperatures and the dissociation of a fraction of such released water molecules into H^+ and OH^- ions. The dissociation energies of four equatorial and two axial H_2O molecules in both the systems have been calculated. The difference in the dissociation energy values have been attributed to the distortions of $M(H_2O)_6$ octahedra. Results obtained for an isomorphous potassium Tutton salt, zinc potassium sulphate hexahydrate are also included.

Keywords. Deaquation; ammonium Tutton salts; dielectric measurements; dissociation energies.

1. Introduction

In recent years, d.c. electrical conductivity measurements have been exploited to study the deaquation processes in some hydrated salts by Kher *et al* (1978), Nandi *et al* (1979) and Singh and Pandey (1980). The electrical measurements also provide an insight into the mechanism of deaquation as to how the groups of H_2O displaced from normal sites in the crystal lattice are kept bound in the structure of the compound up to a certain temperature. At this temperature they are finally released with simultaneous dissociation of a small fraction among them. The undissociated water groups come out rather slowly from the lattice and this phenomenon gets reflected in the thermogravimetric analysis (TGA) study of the salt under consideration.

No such study has, however, been reported for any of the Tutton salts, which are given by the general chemical formula $M''M'_2(XO_4)_2 \cdot 6H_2O$ where M' is a monovalent cation and M'' is a divalent cation with X as S and Se. From the x-ray data as given by Margulis and Templeton (1962), it can be easily observed that the octahedron of water molecules is not exactly regular in a Tutton salt, but rather compressed along the polar axis. In this paper, we report the conductivity (σ), TGA and dielectric constant (ε') studies in zinc ammonium sulphate hexahydrate (zASH) and magnesium ammonium sulphate hexahydrate (MASH) Tutton salts as a function of temperature, and explain the observations in the light of the propositions of Kher *et al* (1978) and the available x-ray data.

* To whom all correspondence should be addressed.

2. Experimental procedure

The ZASH, and MASH Tutton salts were prepared by mixing the corresponding sulphates in equimolar proportion and their single crystals were grown by evaporation of the saturated solutions of the two compounds. Large single crystals with large reflecting faces parallel to (110) plane could easily be grown by this process.

The electrical conductivity as a function of temperature was measured perpendicular to (110) planes using a ECIL EA 815 Electrometer amplifier. The rate of increase of temperature was kept at 1°C/min or 2°C/min in various sets. The dielectric constant was measured using a SIMPSON 901-I RCL Universal Bridge at a fixed frequency of 1 kHz. The TGA was made through a study of the loss in mass of the crystal as a function of temperature, using a sensitive monopan balance (sensitivity 0·1 mg) having an arrangement for suspending the crystal.

3. Results

Figure 1 shows the variation of log σ *vs* temperature for two different heating rates (indicated in the graphs) of ZASH sample in air. As seen from this graph a sharp peak at 98°C and a broad peak at about 137°C are obtained. As the heating rate is increased, the peaks tend to sharpen with increased heights.
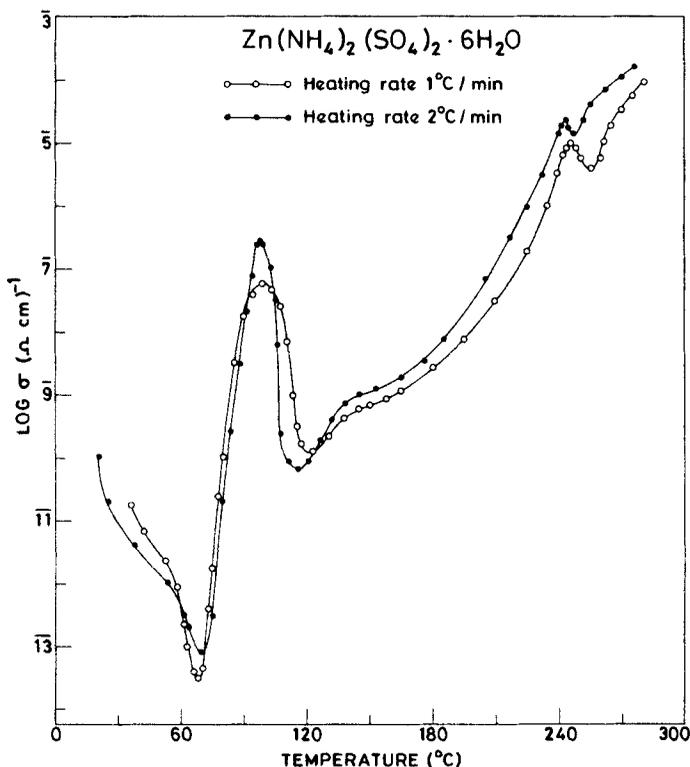
Figure 1. Temperature variation of conductivity of $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ crystal for two different heating rates.

Figure 2 shows the log *I vs* time graph of ZASH sample. This graph is physically important as areas under each of its peaks represent the total mobile charges responsible for electrical conduction at the corresponding peak (transition) temperatures. There is a sufficient justification to name these peak temperatures as transition temperatures because, as concluded later the local arrangement of H_2O groups in a Tutton salt changes at these temperatures.

Figure 3 shows the plot of dielectric constant as a function of temperature, for ZASH sample, the heating rate of sample being kept constant at 1°C/min. As seen from this graph, a sharp peak is observed at 98°C and a broad peak at about 135°C. The positions of these peaks nearly coincide with those of conductivity peaks, thereby indicating the role of a common process for both the physical phenomena.

Figure 4 shows the fractional loss in mass of the ZASH crystal as a function of temperature.

The observations about conductivity, TGA and dielectric constant studies of MASH were almost identical to those for ZASH, and hence, corresponding plots are not shown separately.
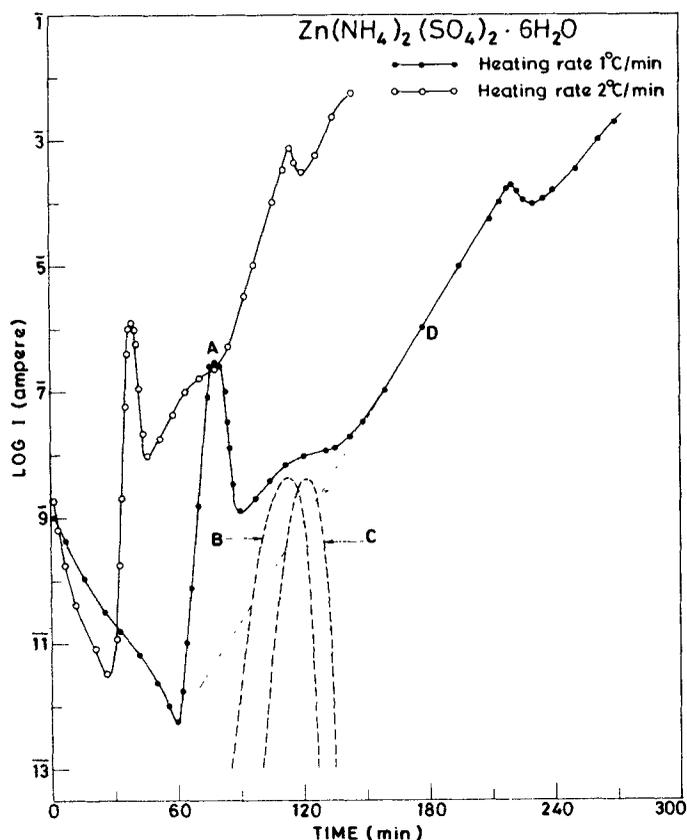

Figure 2. Time variation of current through a crystal of $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ for two different heating rates.
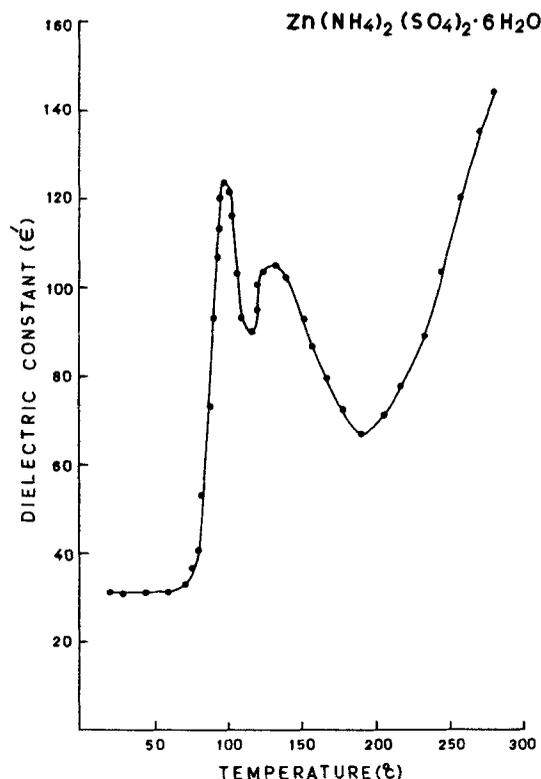
Figure 3. Temperature variation of dielectric constant for $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ crystal.

4. Discussion

To explain the observed temperature variation results, in electrical conductivity and TGA studies of hydrated compounds, Kher *et al* (1978) have proposed a model, according to which the water molecules loosened from their periodic sites in the lattice at a particular temperature are, however, retained in the structure until a much higher temperature. The subsequent attachment of water molecules in the structure is through a random process involving Coulombic attraction of −ve end of H_2O with the surrounding +ve cations. The water molecules are, however, released from the structure when the thermal energy is sufficient for them to break-off their binding in the structure. This further results in dissociation of a fraction of water groups leading to the creation of H^+ and OH^- ions, which contribute towards electrical conduction. The fraction of such dissociated water molecules is obviously given by,

$$f = \frac{n_2}{n_1} = \frac{\displaystyle\int_{(kT+E_d)}^{\infty} E^{1/2} \exp(-E/kT)\, dE}{\displaystyle\int_{kT}^{\infty} E^{1/2} \exp(-E/kT)\, dE}$$

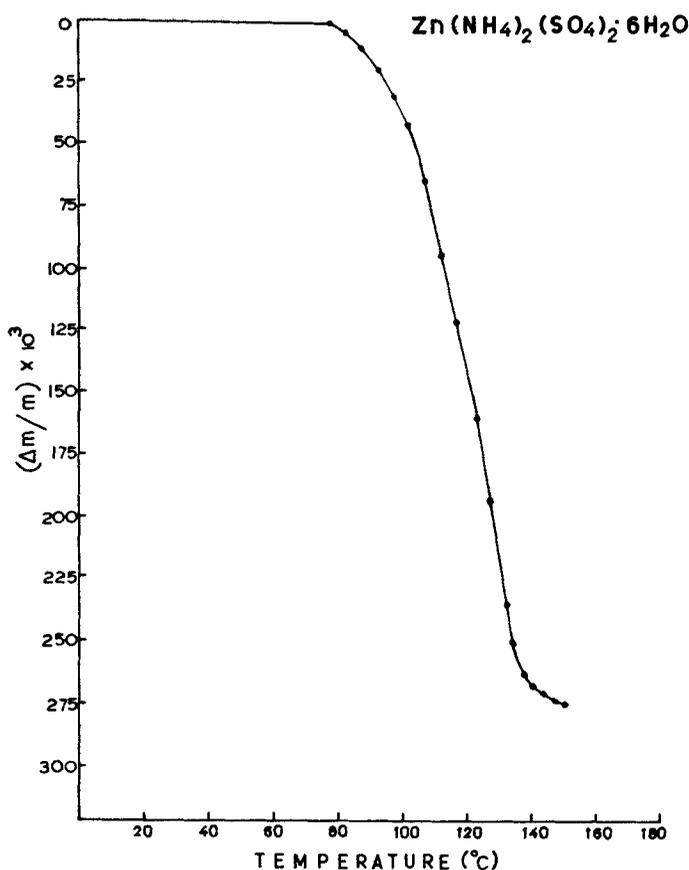where kT is the most probable value of thermal energy at the peak temperature, E_d is the

Figure 4. TGA plot of $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ crystal.

dissociation energy of H_2O trapped in the structure, n_1 is the number of molecules possessing energy greater than kT and n_2 is the corresponding number of molecules with energy greater than $(kT + E_d)$. The E_d value will obviously be less than 1·2 eV, the free ion dissociation energy (Glasstone and Lewis 1960). It would thus be only of academic interest to calculate n_2 chosing E_d as 1·2 eV and for finding a n_2 value close to the experimental value, a lower E_d would have to be searched out.

As already mentioned above, the experimental observations about the two Tutton salts are almost identical, the detailed discussion is therefore given for one of the systems only.

4.1 *Zinc ammonium sulphate hexahydrate*

For ZASH Tutton salt, it is not known, when the H_2O molecules are released from their periodic sites in the lattice. However, the data about different bond-lengths and bond-angles for the water octahedra for this compound are known which are quoted in table 1, and show that the octahedra are not regular with their four equatorial bonds being almost equal but greater than the two nearly equal polar bonds. But this cannot suggest whether the equatorial water molecules will be released earlier or the polar

Table 1. Bond lengths (A) and bond angles (°) in
the water octahedra of ZASH Tutton salt single
crystal.

Bond X–O and Bond angles O–X–O	ZASH
X–O (7)	2·129 (0·012)
X–O (8)	2·117
X–O (9)	2·075
O (7)–O (8)	90·6
O (7)–O (9)	89·1
O (8)–O (9)	89·2

ones. The TGA studies, however, reveal that four water molecules per Tutton salt leave the crystal up to 110°C, indicating that the equatorial water molecules leave the lattice sites at a lower temperature than the polar water molecules. We, therefore, assign the first peak in the conductivity plot to the current due to H^+ and OH^- ions created from four equatorial H_2O molecules and the second peak to such a process involving axial H_2O molecules.

The TGA plot also indicates that all the six H_2O per Tutton salt molecule leave the crystal up to 152°C. The conductivity, however, increases monotonously with temperature even beyond 152°C. This increase should therefore be due to the charge carriers created from ammonium groups. Such a monotonous increase in conductivity has not been observed by us in an isomorphous zinc potassium sulphate hexahydrate (ZPSH) Tutton salt system. The TGA plot of ZASH further indicates that the five H_2O molecules per Tutton salt leave the crystal up to 132°C, and thus suggests that two axial H_2O molecules leave the lattice sites at two different temperatures. The second broad peak, in the conductivity plot of ZASH has accordingly been resolved into two contours marked B (at 130°C) and C (at 137°C), separating simultaneously the contribution (towards conductivity) from ammonium groups.

The fraction f, of dissociated water groups can be determined experimentally, for any of the three conductivity peaks from the area under each of the curves A, B, and C. For the peak A, the kT value comes out to be 0·032 eV, and subsequent calculations with E_d as 1·2 eV yield a very small number of charged particles for this peak than that actually observed. Hence, it appears that the dissociation energy of equatorial water molecules is smaller than 1·2 eV. It is seen that, if we assume the dissociation energy to be 0·27 eV, there is a close agreement with the observed n_2 value. All significant results at different steps of calculations for the three peaks are given in table 2. It is seen that the dissociation energies of two axial H_2O molecules are almost equal and different from that of equatorial H_2O molecules. The conductivity and TGA results are thus in confirmity with the crystal structure data available for this crystal. The difference in the dissociation energies of equatorial H_2O and axial H_2O may be due to the difference in the Coulombic attraction on them.

In the temperature variation of dielectric constant, of ZASH, peaks have been observed at 98°C (sharp) and 135°C (broad). These peaks are attributed to space charge polarization produced by H^+ and OH^- ions, and are expected to be sharp enough as obtained by Singh and Pandey (1980) for $Na_2MoO_4 \cdot 2H_2O$. The observed broadening

Table 2. Significant results at different steps of calculations for the dissociation energy E_d of H_2O molecules in ZASH Tutton salt single crystal.

Parameter	Peaks		
	A	B	C
$T(^\circ K)$	371	403	410
f	2.25×10^{-16}	4.09×10^{-15}	5.88×10^{-15}
$n_2 (E_d = 1.2 \text{ eV})$	8.08×10^4	1.88×10^5	5.88×10^5
n_2 (observed)	4.44×10^{17}	7.75×10^{16}	5.20×10^{16}
Estimated E_d (eV)	0.27	0.30	0.31
Position of H_2O molecule in the octahedra	Equatorial	Axial	Axial

of only the second peak, in the system under study, thus probably indicates that towards the high temperature side the role of charge carriers from ammonium groups is appreciable. It thus also appears to justify our assumption about representing the contribution of ammonium groups in the conductivity plot by a monotonously increasing curve *D*.

4.2 *Magnesium ammonium sulphate hexahydrate*

The data has also been analysed for MASH Tutton salt. The water groups leave the lattice in steps of 4 mol, 1 mol and 1 mol. The apparent dissociation energies of four equatorial water groups is 0.27 eV and that of two axial water groups is 0.30 and 0.31 eV. The two ammonium Tutton salts thus behave identically with regard to the arrangement of water octahedra in them.

For ZPSH, the only potassium Tutton salt, studied so far, the E_d values of all the four equatorial H_2O molecules equals, 0.34 eV, while of the two axial H_2O molecules are different being 0.43 and 0.44 eV. The arrangement of water octahedra in a potassium Tutton salt thus appears to be different from that in ammonium Tutton salt. Crystallographic data about the potassium Tutton salts are however, not available, and it would thus be quite interesting to make such studies so that the above conclusions derived from experiments of electrical conductivity and TGA could be verified.

Acknowledgement

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