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Electrical study of the phase transition in some hydrogen oxalates

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Abstract

The paper deals with accurate measurements of the electrical resistivity ρ and the dielectric constant ε as functions of temperature $300 < T < 450\,\mathrm{K}$ for sodium hydrogen oxalate monohydrate $NaHC_2O_4{\cdot}H_2O$ (**I**) and potassium hydrogen oxalate KHC_2O_4 (**II**). The data obtained revealed the existence of possible structural phase transitions at 342 and 325 K for **I** and **II** respectively.

Thermogravimetric analyses (TGA) of the two compounds have been performed. The thermograms confirmed the absence of any actual loss in weight in the transition temperature regions.

The data are interpreted on the basis of crystal transformation and the arrangement of the molecules in the unit cell including the hydrogen bonding system.

Keywords: Dielectric constant; Oxalate; Resistivity; TGA

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1. Introduction

Sodium hydrogen oxalate $NaHC_2O_4{\cdot}H_2O$ and potassium hydrogen oxalate KHC_2O_4 are members of the hydrogen oxalate series of general molecular formula $MHC_2O_4{\cdot}xH_2O$, where M is a monovalent element and/or group (M is Cs, Rb, Na, K..... and/or NH_4) and x is the number of water molecules ($x = 0, 1, 2, \ldots.$).

The crystal structures of some members of this series, including $LiHC_2O_4{\cdot}H_2O$ [1], $NaHC_2O_4{\cdot}H_2O$ [2–4], KHC_2O_4 [5] and $NH_4HC_2O_4{\cdot}0.5H_2O$ [6,7] were deter-

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mined. Usually, in all these salts, the structure consists of infinite chains of hydrogen oxalate ions joined by asymmetric hydrogen bonds for unhydrated and hydrated molecules. In the case of the hydrated members of this series, the chains are linked transversely in the plane of the hydrogen oxalate ions by weaker hydrogen bonds via the water molecules [1–4, 6, 7].

In addition to the crystal structures of the above mentioned series, those of the related series $(CH_3NH_3)nHC_2O_4$, methylammonium hydrogen oxalates, where n is 1, 2 and 3, were also determined [8–10] as was that of ethyl hydrogen oxalate $C_2H_5HC_2O_4$ [11]. It was found that the hydrogen oxalate ions exhibited a strong tendency to form infinite chains. The geometry of the $HC_2O_4^-$ may thus be expected to respond sensitively to the change in the hydrogen bond environment of the ion chain. A summary of the observed geometries of $HC_2O_4^-$ ions is given by Kuppers [7] and by Thomas and Paramatus [9].

Some physico-chemical properties of $NH_4HC_2O_4 \cdot 0.5H_2O$ have been investigated. For example, the elastic constants [12] and the thermal expansion tensors [13] were measured by Kuppers [12, 13]. An X-ray structural study of the ferroelastic low-temperature phase transition at 145.6 K has been performed by Keller et al. [14]. Much less attention has been devoted to the physico-chemical properties of the other members of this series.

In a series of recent papers [15–20], Abdel-Kader and co-workers have investigated the phase transition in some ammonium salts including ammonium tartrate [15], ammonium purpurate [16, 17], ammonium persulphate [18], sodium hydrogen tartrate [19] and potassium hydrogen carbonate [20] as examples of hydrogen tartrates end hydrogen carbonates through the study of their electrical conductivities and/or relative permittivities as a function of temperature.

Searching for new series of compounds to study, we have chosen the hydrogen oxalate series. In this paper we consider the electrical properties in addition to a thermogravimetric analysis of two members of the above mentioned series, namely sodium hydrogen oxalate (**I**) and potassium hydrogen oxalate (**II**) as representatives of the hydrated and unhydrated salts respectively.

2. Experimental

Both **I** and **II** were Aldrich grade chemicals. Further purification was carried out by recrystallization from redistilled water.

For the electrical measurements, the polycrystalline samples were ground and pressed under a suitable pressure to form discs or pellets, each of diameter ≈ 1 cm and thickness 1.5–2.0 mm. Good contact was achieved by painting both faces of each pellet with air-drying conducting silver paste.

The electrical resistance R was measured using a Keithley type 617 electrometer, and the capacitance C was determined by using an RLC bridge. From the measured values of R and C, in addition to the dimensions of each pellet, the corresponding values of the resistivity ρ, the d.c. conductivity σ and the relative permittivity ε were determined.

A sample holder with brass electrodes was specially designed to carry out the electrical measurements. The temperature of the sample was measured using a digital thermocouple attached to the surface of the sample. The accuracy was better than ± 1 K. The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA7 analyser with a computer interface.

3. Results

3.1. Electrical parameters

3.1.1. Resistivity

Fig. 1(a) shows the variation of the electrical resistivity ρ (in Ω m) as a function of temperature T in the range $330 < T < 400$ K for **I**; the corresponding temperature dependence of the resistivity for **II** is shown in Fig. 1(b). As is clear from Fig. 1(a) and (b), the two plots have nearly the same general character, namely, there is a gradual decrease in the ρ value with increasing temperature up to ≈ 342 K for **I** and up to 325 K for **II**; here, ρ for each salt reaches its minimum value, and beyond this temperature begins to increase again.

The temperature dependence of the dielectric constant ε for **I** and **II** is shown in Fig. 2(a) and (b) respectively. The two plots, as is expected, have the same general feature, namely, the value of ε increases gradually as the temperature increases up to ≈ 343 K for **I** and ≈ 325 K for **II**; the ε value for each salt reaches its maximum value and thereafter decreases with further increase in temperature. When the temperature exceeds 400 K for **I** and 360 K for **II**, the ε value becomes nearly independent of temperature. The occurrence of maxima in the ε vs. T plot for each salt may be an indication of a structural phase change.

The thermogravimetric analysis (TGA) curves of **I** and **II** are shown in Fig. 3(a) and (b). For **I**, no actual loss in weight occurs in the temperature range $300 < T < 380$ K, whereas for **II** the actual loss in weight starts above 370 K. In other words, the two thermograms are characterized by the absence of weight loss in the transition temperature regions.

4. Discussion

Based on the measured electrical parameters represented in this work, one may conclude the existence of a structural phase transition at 342 K for **I** and 325 K for **II**.

The thermograms in Fig. 3(a) and (b) clearly reveal the absence of weight loss in the transition temperature regions. Thus the possibilities of dehydration for **I** and/or some sort of decomposition for **II** are excluded. In other words, the changes in the electrical parameters at the above mentioned temperatures are due to structural phase transition.

The general features of the crystal structures of hydrogen oxalates have been outlined in the Introduction, and here we focus our effort on the detailed structure of the two investigated oxalate salts, namely sodium hydrogen oxalate monohydrate

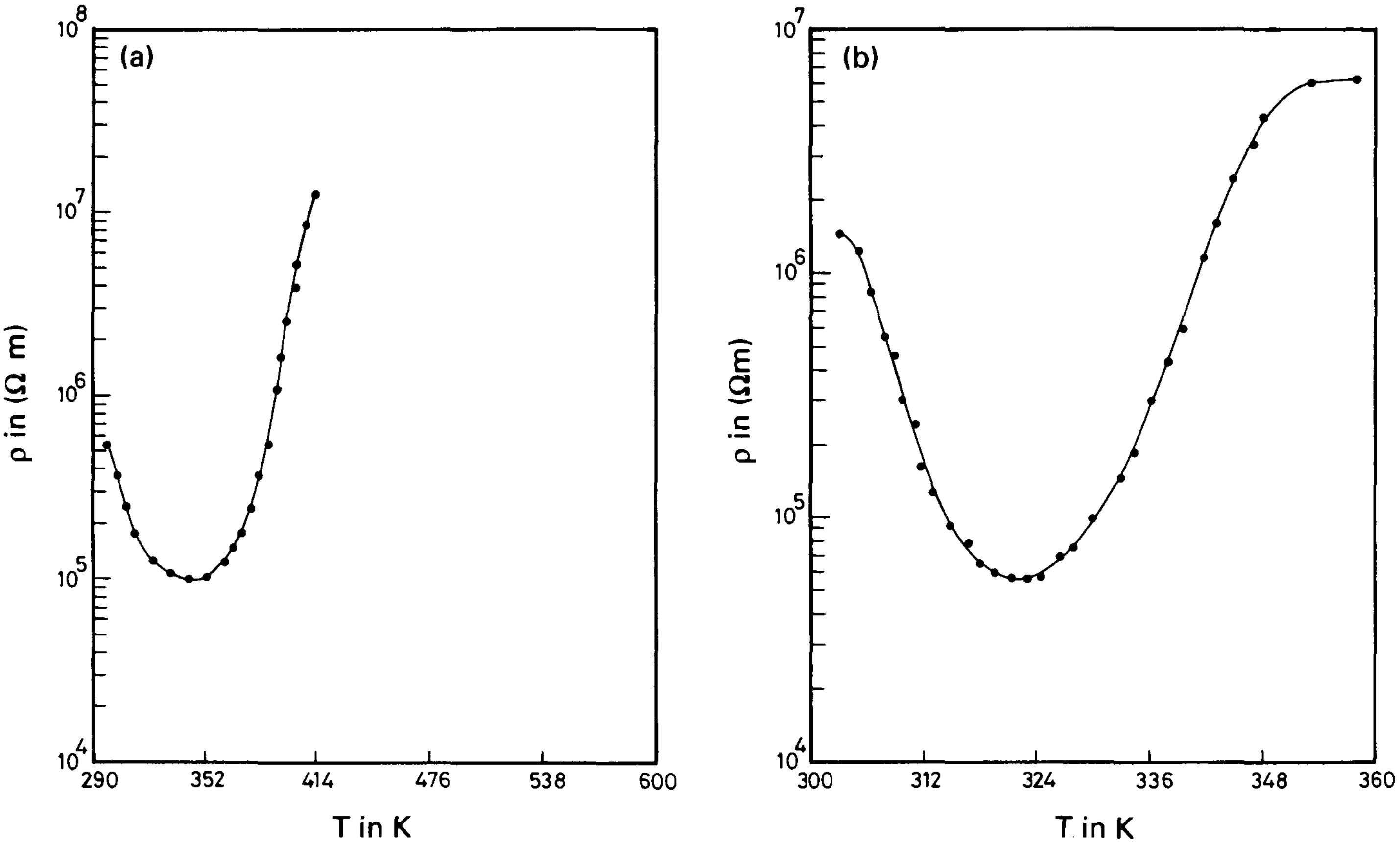

Fig. 1. Variation of the resistivity ρ in Ω m with temperature in K for: (a) sodium hydrogen oxalate monohydrate **I** and (b) potassium hydrogen oxalate **II**.

I and potassium hydrogen oxalate II, in order to illustrate the mechanism of the structural phase change and hence the role of hydrogen bonding in such transition.

For I and according to ref. [3], the crystals are triclinic, PI, with unit cell constants $a = 6.533$, $b = 6.673$ and $c = 5.698$ Å, $\alpha = 85.036°$, $\beta = 109.099°$ and $\gamma = 105.016°$.

The hydrogen oxalate ions (the most important part of the structure) are linked end to end in an infinite chain by hydrogen bonds. The O–H···O distance is 2.571 Å, and the ions are in turn cross-linked via the water molecule by two hydrogen bonds of lengths 2.806 and 2.824 Å and by electrostatic (ionic) bond $Na^+ \cdots O^-$ interaction (each Na^+ ion is surrounded by six oxygen atoms, forming a distorted octahedron). The $Na^+ \cdots O^-$ distance ranges from 2.331 to 2.473 Å. The oxalate group is nonpolar with a dihedral twist of 12.92° about the C–C bond.

For KHC_2O_4, the material crystallizes in space group $P2_1/c$ with $z = 4$. The lattice constants are $a = 4.304$, $b = 12.833$ and $c = 7.632$ Å and $\beta = 102.01°$. The structure is composed of layers of anions and cations. The hydrogen oxalate ions are hydrogen bonded together in an infinite chain with a short hydrogen bond length of 2.524 Å.

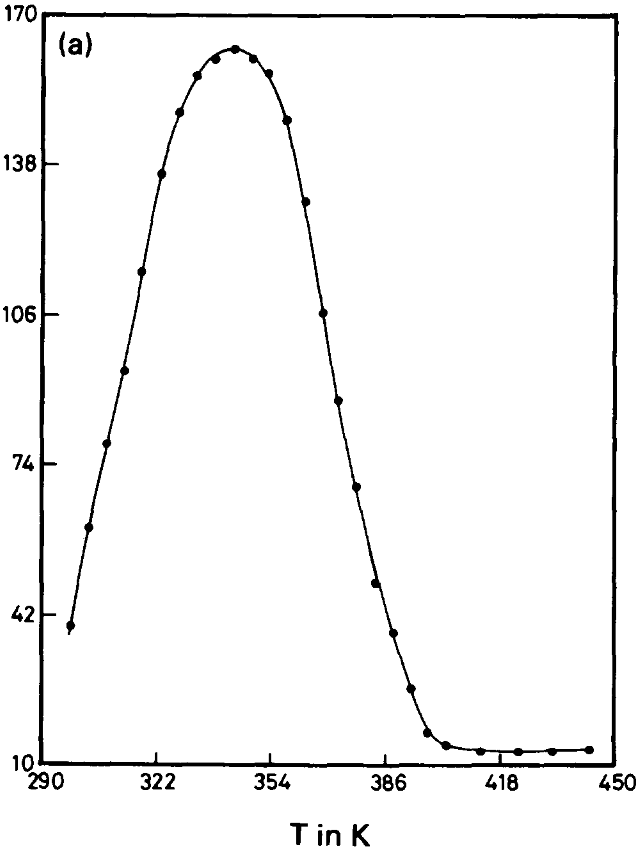

Fig. 2. Temperature dependence of the dielectric constant ε for: (a) I and (b) II.

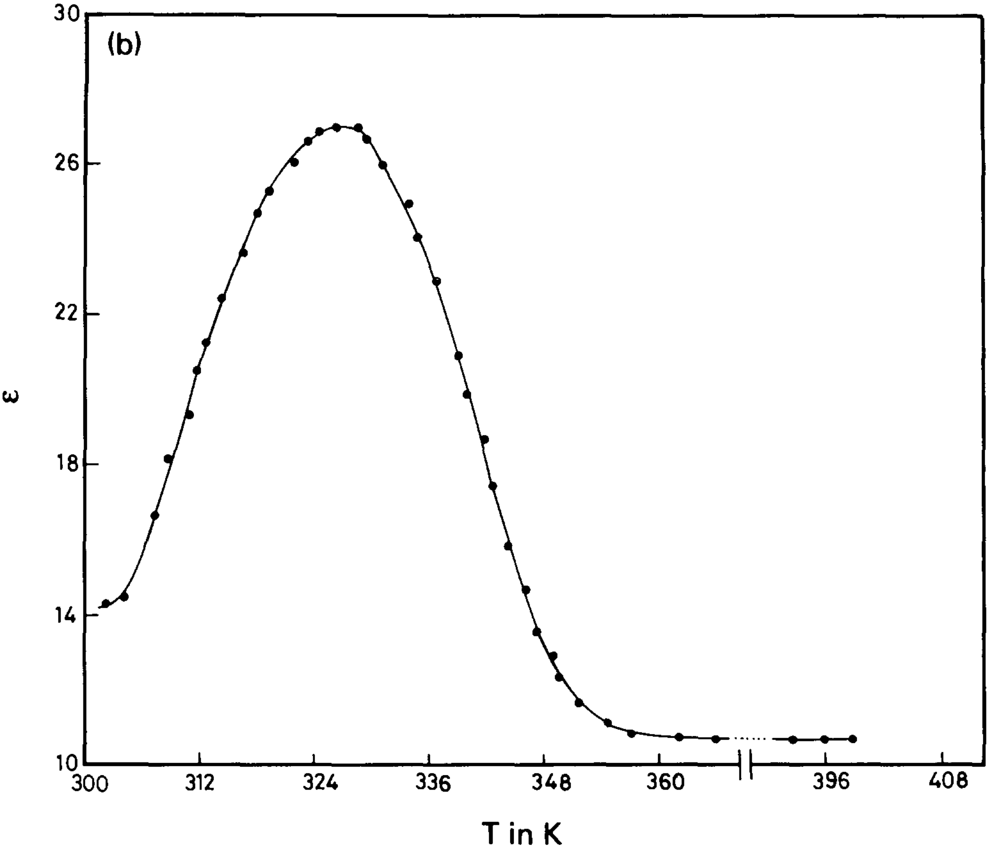

Fig. 2. *(continued)*

Adjacent chains within layers are held together by coordination to a potassium ion. The latter has seven nearest oxalate ions forming a polyhedron of oxygens originating from five different hydrogen oxalate ions at distances from 2.704 to 2.964 Å. In a similar way to the sodium compound, here also the oxalate group is found to be twisted about its C–C bond by an angle of 13.92 ± 0.15°.

Summarizing, both **I** and **II** are hydrogen bonded in their crystalline state and the oxalate ion in the two compounds is twisted by ≈ 12.92° and 13.92° respectively around the C–C bond. As mentioned by several investigators, the change in hydrogen bonding strength (intensity) is usually associated with structural phase change. As an example, the phase transition in ammonium sulphate is not of the order – disorder type but rather involves a change in the hydrogen bonding scheme (N–H···O) [21]. Furthermore, a recent IR spectroscopic study of the structural phase transition in the perovskite-type layer compound $(n\text{-}C_{16}H_{33}HN_3)_2CoCl_4$ showed that the occurrence of a structural phase transition is related not only to the dynamics of the alkylammonium ions but also to the change in the strength (intensity) of the N–H···Cl

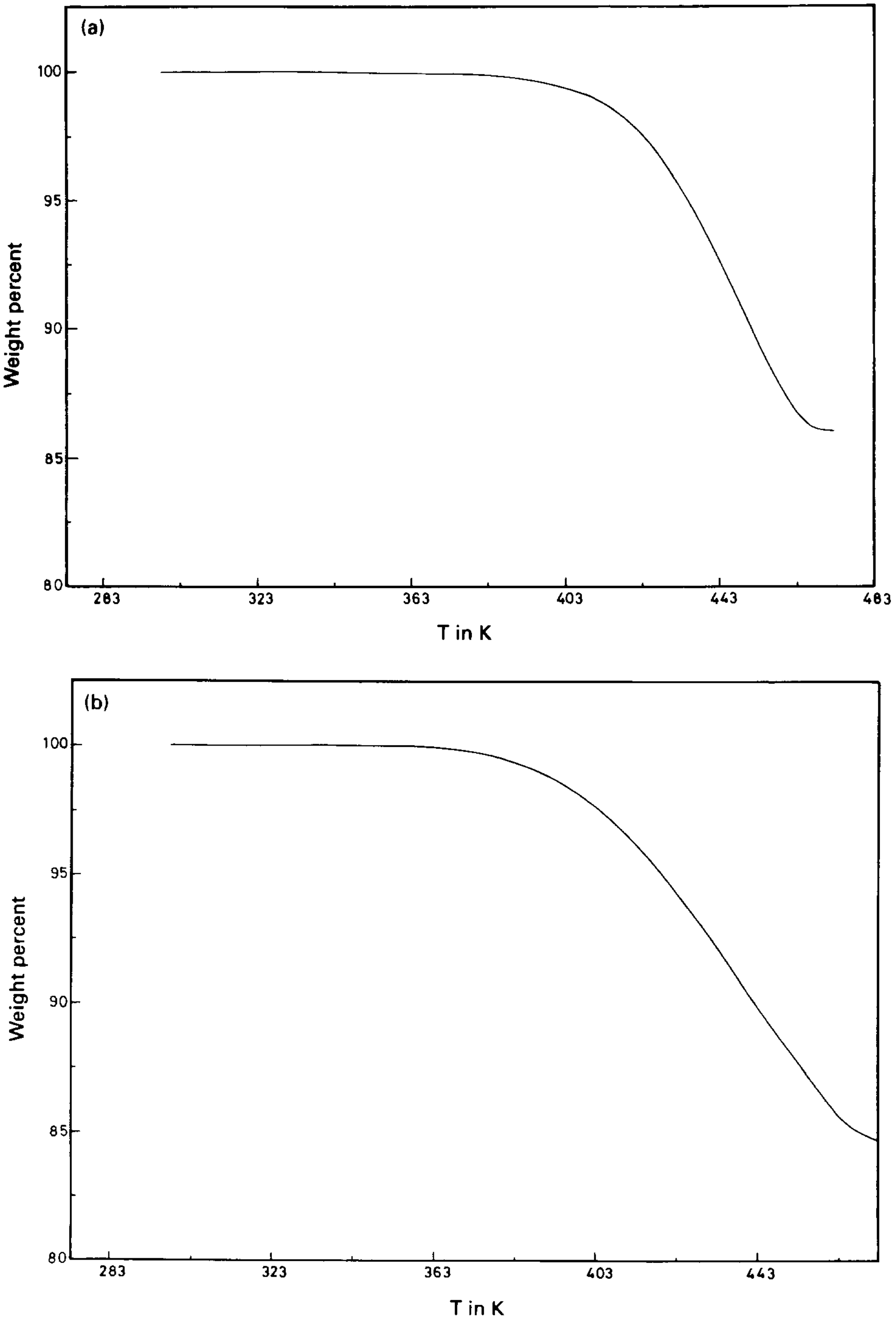

Fig. 3. Thermogravimetric analysis (TGA) curves for: (a) **I** and (b) **II**.

hydrogen bonds through each phase transition. Thus the phase transition in each case not only involves an order–disorder phase transition, but is also accompanied by a change in the intensity of the N–H···Cl hydrogen bond [22].

In the present case of the two oxalate compounds **I** and **II**, a similar mechanism may exist. Thus, as the temperature increases and approaches 342 K for **I** and 325 K for **II** the thermal energy corresponding to this temperature may be enough to change the intensity of the hydrogen bonding scheme in **I** and/or **II**. The weakening of the hydrogen bonding will be associated with the reorientational motion of the hydrogen oxalate molecules and therefore rearrangement of the structure as a whole, and this will lead to the observed phase transition in each salt. Furthermore, as mentioned above, the Na^+ and/or K^+ ions are coordinated by oxygen atoms and therefore some kind of ionic and or/ electrostatic forces of the type $M^+ \cdots O^-$) may arise, where M^+ denotes Na^+ or K^+. The strength of these forces will vary as the salt is supplied with thermal energy and could subsequently lead to some rearrangement of the hydrogen oxalate ions and of the molecule as a whole, resulting in the observed phase transitions at the above noted temperatures. In the future, other techniques such as high temperature X-ray analysis, nuclear magnetic resonance (NMR) and/or Raman spectroscopy will be needed in order to confirm the observed phase transition . Unfortunately such techniques are not available in our laboratory at present.

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