Accepted Manuscript

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PII: S0925-8388(16)30378-4

DOI: 10.1016/j.jallcom.2016.02.110

Reference: JALCOM 36728

To appear in: Journal of Alloys and Compounds

Received Date: 7 January 2016

Revised Date: 11 February 2016

Accepted Date: 12 February 2016

Please cite this article as: S. Guidara, H. Feki, Y. Abid, High-temperature dehydration behavior and ionic conduction of 2,5-dimethylanilinium chloride monohydrate, *Journal of Alloys and Compounds* (2016), doi: 10.1016/j.jallcom.2016.02.110.

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High-temperature dehydration behavior and ionic conduction of 2,5-dimethylanilinium chloride monohydrate

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Abstract

The 2,5-dimethylanilinium chloride monohydrate compound is obtained by slow evaporation at room temperature. This material is characterized by DSC, X-Ray powder diffraction, Raman and impedance spectroscopy technique measured in the $2.10^2 - 5.10^6$ Hz frequency and 292–422 K temperature ranges. The calorimetric study has revealed three endothermic peaks at 355 K, 392 K and 403 K which defines four successive phases denoted I, II, III and IV. The first peak corresponds to water escape from the crystal. After heating above 355 K, the compound dehydrates and the crystal space group changes from non-centrosymmetric to centrosymmetric symetry. The activation energy responsible for dielectric relaxation extracted from the modulus spectra is found to be almost the same as the value obtained from temperature variation of dc conductivity for phases I and IV. These results indicate that the transport is through ion hopping mechanism. The influence of the dehydration process on the compound conductivity was also discussed.

Keywords: Calorimetric study, Dehydration, Impedance spectroscopy, Dielectric properties.

1. Introduction

Semi organic materials have attracted intensive interests owing to their potential applications in data storage, signal processing, sensing, rewriteable optical data storage, etc. [1-3]. These materials are not only very important for having the potential for a large range of optical properties such as efficient luminescence and second-order non-linear optical activity [4-7], but

also favorable for studying the structure–property relationship [8]. Furthermore, few electrical and dielectrical studies of these compounds have been reported. This work is a continuation of our interest in 2,5-dimethylanilinium derivatives. Our last three published papers have been devoted to the X-ray diffraction and vibrational studies as well as DFT calculations of nonlinear optical compounds, 2,5-dimethylanilinium chloride monohydrate [9], 2,5-dimethylanilinium dihydrogen phosphate [10] and bis 2,5-dimethylanilinium sulfate [11]. As an extension of our searches for exploring new properties concerning hybrid salts, we report a detailed investigation of the thermal, electrical and dielectrical behavior of the 2,5-dimethylanilinium chloride monohydrate compound. The crystal structure of this compound was elucidated by W. Smirani et al. involving water molecules [12]. In order to determine the effect of the water molecules escape on ionic conduction, we have made many investigations. The techniques used include differential scanning calorimetry (DSC), X-ray powder diffraction, impedance and Raman spectroscopy at several temperatures. This combination of techniques allowed us to characterize in detail physical properties of this compound and correlated them with the structural changes in the crystal accompanying the dehydration process.

2. Experimental procedure

The title compound was synthesized from an ethanolic solution of 2,5-dimethylaniline and hydrochloric acid in equimolar amounts. The obtained solution was left to stand at room temperature until formation of colorless single crystals of 2,5-dimethylanilinium chloride monohydrate (2,5-DACM) [9]. Structural information at room temperature has been mentioned elsewhere [12]. In summary, the title compound crystallizes in the monoclinic system with the non centrosymmetric space group P2₁ (Z=2) with a = 7.529(3)Å, b = 7.452(2)Å, c = 9.032(4)Å and β = 102.830(4)°. From single crystal XRD data, it is observed that the asymmetric unit of the title compound is built up from one chloride anion CI⁻, one 2,5-dimethylanilinium cation [2,5-(CH₃)₂C₆H₃NH₃]⁺ and one water molecule. The crystal packing is determined mainly by N-H...O, N-H...Cl and O-H...Cl hydrogen bonds. The thermal behavior of this compound was investigated by differential scanning calorimetry using a DSC (Q-100) TA Instrument in the 250-450 K temperature range with scanning rate 5°C/min under N₂ atmosphere. X-ray powder diffraction pattern was recorded in a Philips PW 1710 diffractometer operating with copper radiation K α = 1.5418 Å for the 2 θ angular range of 5-60°. Unit cell parameters of the

synthesized compound were refined by Rietveld method from powder data. The impedance spectroscopy was performed on pellet disks of about 5 mm diameter and 1.5 mm thickness. The electrical impedances were measured at a frequency ranging from 200 Hz to 5 MHz with a NOVOCONTROL system integrating ALFA dielectric interface. The measurements were carried out at temperatures in the range 292–422 K.

3. Results and discussion

3.1. Calorimetric study

The DSC measurement of 2,5-DACM were performed on heating a sample (2.9 mg mass) with scanning rate 5 °C/min in the 250-450 K temperature range. The thermal analysis result is reported in Fig. 1. This unambiguously shows the existence of three heat anomalies at T_1 =355 K, T_2 =392 K and T_3 =403 K, respectively, which defines four successive phases denoted I, II, III and IV. Peak 1 describes a process which is associated with water molecules escape from the crystal. Interestingly, this dehydration is also observed in a quite similar compound, 2,3-dimethylanilinium hydrogen sulfate monohydrate, at nearly the same temperature [13]. According to visual observation of the dehydration crystal on heating stage, the white product covered the whole surface in the early stage of dehydration.

3.2. Structural analysis

In order to determine the structural changes in the crystal accompanying the dehydration process, we have performed X ray powder measurement. The sample was heated up to 370 K and then was cooled to room temperature. The obtained XRD pattern is shown in Fig 2. The Rietveld refinements data performed using FULLPROF program [14] revealed that the 2,5-dimethylanilinium chloride (2,5-DAC) crystallized in the monoclinic structure with the centrosymmetric P2₁/m space group with a = 18.845Å, b = 5.203Å, c = 17.041Å and β = 91.157° with a reliability factor χ^2 =3.68. The comparative graphs of X ray powder patterns of both hydrate and dehydrate compound are given in Fig. 3. Described above changes are due to the dehydration process corresponding to water vanishing from the crystal. The water escape was preceded by a weakening of the hydrogen bonds in which the water molecules were involved.

3.3. Temperature evolution of the Raman spectra

It is of interest to observe the possible changes in the Raman bands corresponding to characteristic vibrations of the molecules at different temperatures, so we have undertaken a Raman study between 298 and 358 K. It is necessary to mention that the detailed assignment of the IR and Raman bands at room temperature is given in our previous work [9]. The recording of the Raman spectra versus temperature (Fig. 4) in the range 3600-2700 cm⁻¹ shows that the most significant change is related to the vanishing of the intense band observed at 3390 cm⁻¹ assigned to stretching O-H of water molecule which is related to the removal of water from the crystal lattice and confirms the above conclusion.

3.4. Dielectrical study

The study of the dielectric properties is an important source for valuable information about the mechanisms of conduction in the materials and the origin of the dielectric relaxation. The complex dielectric function is expressed as:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad (1)$$

where ε' and ε'' are the real and imaginary part of the dielectric constant, respectively. The temperature dependence of the relative dielectric constant of the ε'_r and ε''_r (200 Hz – 220 kHz) of the title compound are shown in Fig. 5. These spectra present a prominent dielectric peak at T=362 K associated to the dehydration process corresponding to the peak centered at T₁ = 355 K in the thermogram. This temperature does not change with increasing frequency, suggesting that the sample does not present any type of relaxation in the frequency range. The dielectric constant decreases with the increase in frequency, which is a general characteristic of a dielectric material. This is due to the absence of dipolar and ionic polarizations in the material at a higher frequency [15].

3.5. Impedance spectroscopy

The complex impedance spectra of title compound are shown in Fig. 6. In the studied frequency range and for all measured temperature excepting dehydration temperature region, one relaxation peak is observed revealing that the single semicircular response is from grain interior and no grain boundaries are involved, which indicates departure from the ideal Debye behavior [15]. In the temperature range between 352-372K, the impedance spectra mainly consists of two parts: a high frequency region due to the ionic conduction of 2,5-DACM pellet and a low-frequency region characterized by a straight line due to a surface layer effect. A careful analysis of the

thermal evolution of the complex impedance spectra shows that there is an increase of the value of (-Z") in each phase, which is in good agreement with the calorimetric study. As temperature increases, the radius of the arc corresponding to the bulk resistance of the sample decreases for each phase, indicating an activated thermal conduction mechanism. It is worth to note that the material shows an unusual response from hydrated to dehydrated state. A deviation from the Arrhenius behavior was observed surrounding the dehydration process with the impedance spectra increasing due to the heat-induced removal of inter-layer water. This process corresponding to the loss of water is accompanied by an important decrease of conductivity. Such behavior was observed in many other compounds [16,17].

3.6. Complex modulus analysis

Modulus formalism is generally used to analyze dielectric relaxation. The complex electric modulus M is defined by the reciprocal of the complex permittivity ε^* (M* = 1/ ε^*) [18] and corresponds to the relaxation of the electric field in the system when the electric displacement is constant. So from the electric modulus, we can represent real dielectric relaxation process admitted as:

$$M^* = M' + jM''$$
(2)

where M' and M" are the real and imaginary parts of complex modulus.

Fig. 7 represents the real M' variation against angular frequency of 2,5-DACM at some temperature. In the low frequency region, the magnitudes of M' tend to zero and coincide with each other and at high frequencies, all the curves attain to asymptotic form and reach a constant value, which confirms a negligibly contribution of electrode effect. In the other frequency region, the value of M' has followed a continuous dispersal with increase in frequency which may be caused by short range mobility of charge carriers.

In order to determine some characteristic parameters of the charge carriers such as their activation energy and relaxation frequency, numerical simulations of the modulus spectra are interesting. Bergman has proposed:

$$M''(\omega) = \frac{M''_{max}}{(1-\beta) + \left(\frac{\beta}{1+\beta}\right) \left[\beta \left(\frac{\omega_{max}}{\omega}\right) + \left(\frac{\omega}{\omega_{max}}\right)^{\beta}\right]}$$
(3)

where M''_{max} and ω_{max} is the peak maximum and peak angular frequency of imaginary part of the modulus, respectively. β is the well-known Kohlrausch parameter. This parameter characterizes

the degree of non-Debye behavior which decreases with the increase in the relaxation time distribution ($0 \le \beta \le 1$). Fig. 8 represents the frequency dependence of M"(ω) recorded at T=342K with fitting. The normalized imaginary part M"/M"_{max} as a function of angular frequency is shown in Fig. 9. The plots show a slightly asymmetric peak at each temperature. This peak shifted towards higher relaxation frequencies with increasing temperature for each phase indicating a correlation between the motions of mobile charge carriers [19].

Frequency relaxation $f_p = \frac{\omega_{max}}{2\pi}$ was determined from fitting M" using the above equation, which is thermally activated and could be expressed as:

$$f_{p} = f_{0} \exp\left(-\frac{E_{a}}{k_{B}T}\right)$$
(4)

where E_a is the activation energy and f_0 is a pre-exponential factor and k_B is the Boltzmann's constant. A plot between $Ln(f_p)$ and 1000/T is shown in Fig. 10, which is well described by Arrhenius equation. A change of the curve slope is noted at T_1 , T_2 and T_3 , which confirms the DSC study.

Fig. 11 shows the imaginary part of the electrical modulus M'' as a function of the real part M' at T=342K. In the studied frequency range, single relaxation peak was observed which is associated with grain effect.

In order to distinguish whether the short range or long range movement of charge carries is dominant in a relaxation process [20] we have presented the combined plot of M" and -Z" versus frequency at T=342K in Fig. 12. The separation of peak positions of M" and -Z" suggests that the relaxation process is dominated by the short range movement of charge carriers and departs from the ideal Debye type behavior while the frequencies coincidence suggests the long range movement of charge carriers is dominant [21-23].

3.7. Electrical conductivity

Electrical conductivity in the material is due to the ordered motion of weakly bound charged particles under the influence of an electric field and it is a thermally activated process. It is one of the significant properties of the materials to be characterized depending on the nature of charge carriers dominating the conduction process such as electrons/holes or cations/anions.

3.7.1. AC Conductivity

The phenomenon of the conductivity dispersion is generally analyzed using jonscher's universal power law [24].

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \tag{5}$$

with σ_{dc} is the value of the conductivity at low frequency, A is a factor dependent on temperature and s is an exponent function of temperature (0<s<1). The exponent s represents the degree of interaction between mobile ions and the environments surrounding them.

The frequency variation of the ac conductivity, $\sigma_{ac}(\omega)$ for 2,5-DACM compound at T=342K is shown in Fig. 13 (inset). The conductivity results are fitted by the above equation (eq. 5) and presented with solid line. At high frequencies, the conductivity shows dispersion pattern which is a characteristic of ω^s , whereas the frequency independent plateau region at low frequencies corresponds to DC conductivity of the material.

The hopping frequency ω_h of the charge carriers which represents the crossover frequency from dc to dispersive conductivity region at $\omega > \omega_h$ can be calculated by the following expression:

$$\omega_{\rm h} = \left(\frac{\sigma_{\rm dc}}{\rm A}\right)^{1/\rm s} \tag{6}$$

The hopping frequency is temperature dependent and it obeys the Arrhenius equation:

$$\omega_{\rm h} = \omega_0 \exp\left(-\frac{E_{\rm a}}{k_{\rm B}T}\right) \tag{7}$$

where ω_0 is the pre-exponential of hopping frequency and E_a the activation energy for the hopping frequency [25]. Fig. 14 shows the variation of $Ln(\omega_h)$ versus (1000/T). It shows an Arrhenius-type behavior. The activation energies obtained from straight's slopes line segments are E_{aI} =3.14 eV, E_{aII} =4.74 eV and E_{aIV} =0.75 eV.

Conductivity master curves for several temperatures for the title compound are shown in Fig. 13. AC conductivity can be expressed by a function with a non-dimensional frequency by the following scaling from:

$$\frac{\sigma_{ac}(\omega)}{\sigma_{dc}} = F\left(\frac{\omega}{\omega_{h}}\right) \qquad (8)$$

In this scaling process, the ac conductivity axis is scaled by σ_{dc} and the frequency axis by ω_h , σ_{dc} is a parameter obtained from the fit of the conductivity as a function of angular frequency. Scaling the conductivity spectra in this way at different temperatures merges on a single curve which implies that the relaxation dynamics of charge carriers is independent of temperature.

3.7.2. DC Conductivity

DC conductivity data are plotted in Arrhenius format as $Ln(\sigma_{dc}T)$ versus (1000/T) (Fig. 10) described by:

$$\sigma_{dc}T = Bexp\left(-\frac{E_a}{k_BT}\right)$$
 (9)

where B is a pre-exponential factor, k_B the Boltzmann's constant and E_a is the thermal activation energy of ion migration.

Fig. 10 identified four regions. Regions (I), (II) and (IV) correspond to an Arrhenius type behavior. The activation energy calculated from linear fit to the data points is $E_{a I} = 2.82 \text{ eV}$ in the hydrated compound, $E_{a II} = 0.48$ eV and $E_{a IV} = 0.62$ eV for dehydrated compound. Activation energies values obtained from the analysis of modulus, conductivity data and hopping frequency are close for phases I and IV. These results indicate that the transport is through ion hopping mechanism in the investigated sample at these phases. In order to determine which ion is responsible for the hopping mechanism of the title compound in its hydrated form, let's have a look into the structure arrangement. So, we have presented in Fig. 15 the atomic arrangement projection along the a axis of the title compound. From the single crystal XRD data, the crystal packing can be described as a typical layered organization. A projection of such a layer shows that the Cl⁻ anions are linked to the water molecules by O—H…Cl hydrogen bonds to form infinite corrugated chains along the b direction (Fig. 15). These chains are themselves connected via N—H…O and N—H…Cl hydrogen bonds originating from NH₃⁺ groups, so as to built inorganic layers spreading around the (a,b) plane [12]. From the structure disposition and since the chloride anion is 3.48 times lighter than the 2,5-dimethylanilinium cation, we can deduce that the conductivity in this sample in its hydrated form is may be assured by the contribution of the movements of anionic parts along the b-axis.

4. Conclusion

The 2,5-dimethylanilinium chloride monohydrate compound was studied at various temperatures with the help of DSC, XRD, Raman and impedance measurements. DSC curve shows an intense peak at about 355K which corresponds to water escape from the crystal. After heating above 355K the compound dehydrates and the crystal space group changes from non-centrosymmetric (P2₁) to centrosymmetric (P2₁/m) space group, while maintaining the same system. Impedance spectroscopy was used to characterize the electrical and dielectrical behavior of this material in its both hydrated and dehydrated forms as a function of frequency at various temperatures. It

makes clear that during the heating process and near the dehydration temperature, the radius semicircles of the Cole-Cole spectra increase significantly, which corresponds to the loss of water, reflecting the perturbation of the ion transport mechanism at this temperature range. The near value of activation energies obtained from the modulus, conductivity data and hopping frequency confirm that the transport is through ion hopping mechanism in the sample for phases I and IV. From the hydrated compound structure, the transport is probably dominated by the motion of anionic parts "Cl⁻" along the "b" direction.

Acknowledgment

The authors thank the Unity of Raman Spectroscopy at Faculty of Sciences of Sfax, Tunisia for Raman measurements.

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Figure 1: Differential scanning calorimetry diagram of 2,5-DACM compound.



Figure 2: X-ray powder diffraction pattern of 2,5-DAC.



Figure 3: X-Ray powder diffraction of 2,5-DACM and 2,5-DAC measured at room temperature.



Figure 4: Temperature evolution of the Raman spectra in the 3600-2700 cm⁻¹ wavenumbers

range.



Figure 5: Temperature dependence of ϵ'_r and ϵ''_r for 2,5-DACM before and after dehydration.



Figure 6: The Cole–Cole plots at different temperature of 2,5-DACM before and after dehydration.



Figure 7: Angular frequency dependence of M' at some temperatures of 2,5-DACM compound.



Figure 8: Angular frequency dependence of M" at T=342K for 2,5-DACM.



Figure 9: Angular frequency dependence of M" at several temperatures.



Figure 10: Dependence of $Ln(\sigma_{dc}T)$ and $Ln(f_p)$ on reciprocal temperature.



Figure 11: The Variation of M" as a function of M' at T=342K.



Figure 12: The M" and (-Z") spectra at T= 342 K of 2,5-DACM.



Figure 13: Conductivity master plot in the 292-422 K temperature range. (**inset**): Angular frequency dependence of the AC conductivity at T=342K fitted using Jonscher's law.



Figure 14: Temperature dependence of the hopping frequency.



Figure 15: Projection along the a axis of the atomic arrangement of 2,5-DACM [12].

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Highlights

- ► The calorimetric study of 2,5-DACM has revealed three endothermic peaks.
- ► The dielectrical properties were studied using the impedance measurements.
- ► The X ray powder diffraction has been performed.
- ► The mobility of the charge carriers was reported and discussed.