

## Electrical conductivity in new imidazolium salts of dicarboxylic acids

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Electrical conductivities of powder samples of five new imidazolium salts of aliphatic dicarboxylic acids (imidazolium malonate (1), imidazolium glutarate (2), imidazolium adipate monohydrate (3), diimidazolium suberate (4), imidazolium sebacate (5)) were measured by impedance spectroscopy as a function of temperature. It was found that conductivities increase with temperature. At high temperatures, the lowest conductivity was determined for imidazolium glutarate ( $10^{-5}$  S/m) and the highest – for imidazolium sebacate ( $10^{-1}$  S/m). The correlation between crystal structures of the investigated salts and their ionic conductivities is discussed.

Key words: *electrical conductivity; imidazolium salt; dicarboxylic acid*

### 1. Introduction

Imidazole is a nitrogen heterocycle of paramount importance, with special biological properties. The imidazole moiety serves as a proton transfer agent in living systems due to its molecular structure, which allows imidazole to act as a weak acid and as a base. Recently, such properties have been used to design conducting electrolytes for highly efficient fuel cells operating at high temperatures [1].

For the first time, conductivity in pure crystalline imidazole was determined by Kawada et al. [2] and Chojnacki et al. [3]. The ionic conductivities of these materials were explained by the Grotthus model [4]. The imidazole molecule enables the formation of proton defects and provides a fluctuating donor/acceptor function. Furthermore, *ab initio* calculations have showed that hydrogen bonds between imidazole molecules are characterised by a low proton transfer barrier [5].

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Kreuer et al. [6] measured electrical conductivity of strong inorganic acids doped with imidazole in the liquid state and analysed the role of this compound in ionic conductivity. It was noticed that the addition of the basic imidazole molecule causes a number of proton defects in  $\text{HSO}_4^-$  and  $\text{H}_2\text{PO}_4^-$  anions.

In our study, we have obtained and examined new imidazolium salts of aliphatic dicarboxylic acids in the solid crystalline state. The main task of this work was to determine the conductivity and attempt to find a correlation between the ionic conductivities and structures of the obtained crystals.

## 2. Experimental

*Synthesis and crystallisation.* Imidazole and dicarboxylic acids were dissolved separately in anhydrous ethyl acetate and then the solutions were mixed together and stirred until a white precipitate appeared. The reaction product was separated and washed with anhydrous ethyl acetate. The starting materials, approximately 99% pure, obtained from Sigma-Aldrich and Fluka, were used without further purification. The crystallisation of all salts was carried out by evaporating the solvent.

*Conductivity measurements.* The samples of each salt in the form of a powder were pressed at room temperature under  $p = 50$  MPa for  $t = 20$  min. The samples, 1.5–2.5 mm thick and 13 mm in diameter, were covered with silver paste electrodes. The real and imaginary parts of electrical impedance were measured in the frequency range from 100 Hz to 1 MHz by means of a computer-controlled HP-4284A precision LCR meter. The temperature of the samples was stabilized using a CF 1204 Oxford Instruments cryostat, equipped with an ITC4 temperature controller. Data collection for a number of frequencies from the above range was performed after the temperature of the sample was stabilized. The dc resistivity of imidazolium glutarate was directly measured using a Keithley electrometer.

## 3. Results and discussion

Electrical conductivity measurements were carried out by impedance spectroscopy for tablets made as described above for imidazolium malonate (**1**), imidazolium glutarate (**2**), imidazolium adipate monohydrate (**3**), diimidazolium suberate (**4**), and imidazolium sebacate (**5**). A typical dependence of the imaginary part of impedance  $Z''$  on the real part  $Z'$  (Argand diagram) for diimidazolium suberate is shown in Fig. 1.

Such a dependence (one semicircle tending to ( $Z' = 0$ ,  $Z'' = 0$ ) with increasing frequency) is expected when the equivalent circuit of the sample is composed of one resistivity  $R$  and one parallel capacity  $C$ . The dc resistivity of the sample can be estimated as  $Z' = R$  when the frequency  $f \rightarrow 0$ .

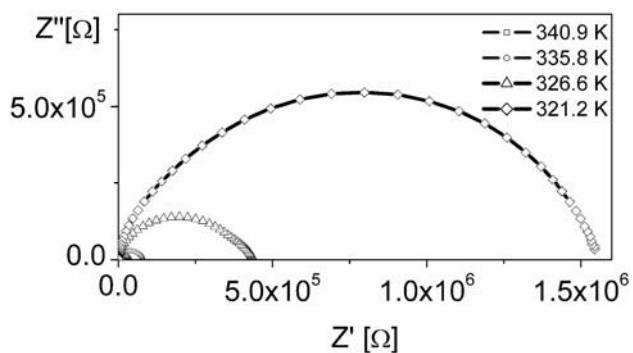
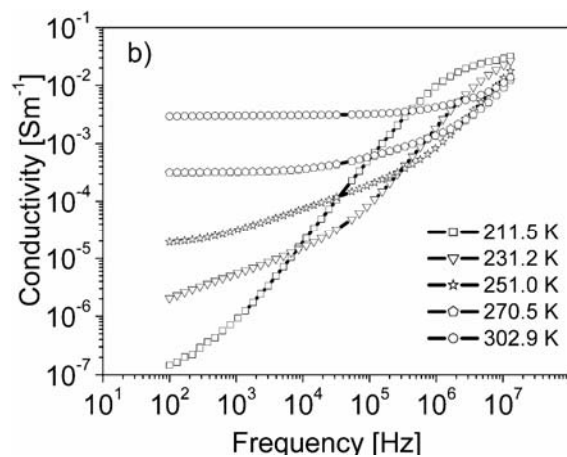
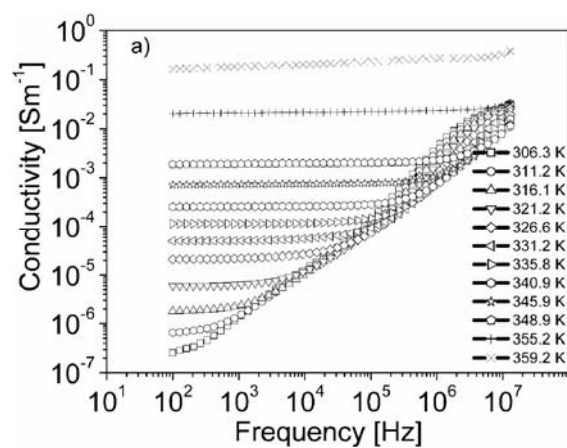


Fig. 1. Argand diagram for diimidazolium suberate

The frequency dependences of ac conductivity ( $\sigma_{ac}$ ) for all the compounds are shown in Figs. 2a–e. The dc conductivity  $\sigma_{dc}$  for a given temperature can be read out from the low frequency plateau of each  $\sigma_{ac}(f)$  curve.



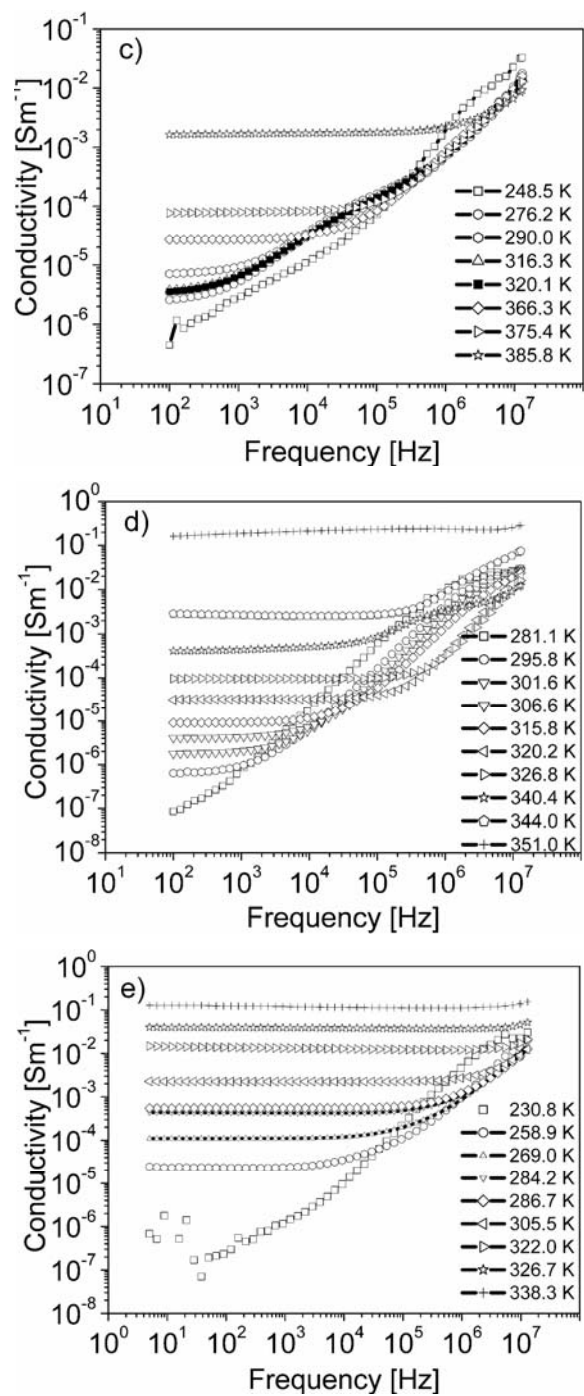


Fig. 2. Frequency dependences of ac conductivity for the investigated salts: a) diimidazolium suberate, b) imidazolium suberate, c) imidazolium glutarate, d) imidazolium adipate, e) imidazolium sebacate

The Arrhenius dependence:

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where  $E_a$  denotes the activation energy,  $\sigma_0$  the pre-exponential factor, and  $k$  the Boltzmann constant, is fulfilled in all cases. The Arrhenius plots  $\sigma_{dc}(1/T)$  obtained from the ac results for all compounds are displayed in Fig. 3. The activation energies calculated from the Arrhenius formulae are presented in Table 1.

Table 1. The activation energies for imidazolium salts of dicarboxylic acids

Compound	Activation energy [eV]
Imidazolium malonate (1)	0.75
Imidazolium glutarate (2)	0.70
Imidazolium adipate hydrate (3)	1.06
Diimidazolium suberate (4)	1.52
Imidazolium sebacate (5)	1.68

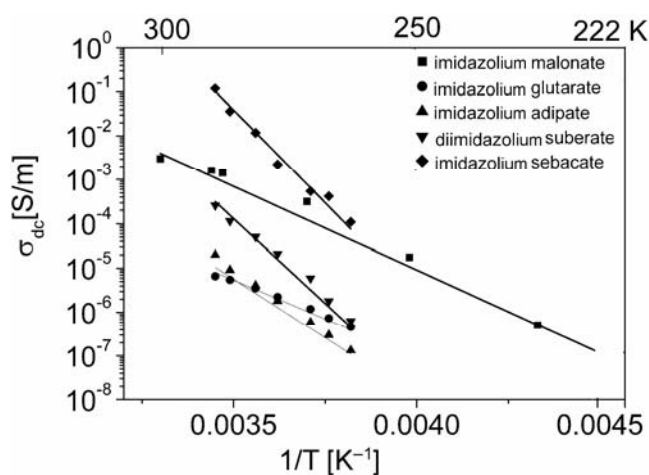


Fig. 3. Arrhenius plot of  $\sigma_{dc}$  for all the investigated compounds

In the case of imidazolium glutarate, the ac conductivity is compared with direct dc measurements (Fig. 4). Both results are in a good agreement.

The activation energies presented in Table 1 may be correlated with the crystal structures of the investigated salts. The crystal data concerning the investigated imidazolium salts are listed in Table 2.

The characteristic feature of the investigated imidazolium salts is that in all (1–5) the crystal structures, imidazolium cations and dicarboxylic anions are connected by hydrogen bonds of the N-H $\cdots$ O type, forming in flat ribbons. These ribbons are arranged in two-dimensional layers (see Fig. 5). In these two-dimensional hydrogen

Table 2. Crystal data of imidazolium salts

Property	Compound				
	Imidazolium malonate (1) [8]	Imidazolium glutarate (2)*	Imidazolium adipate monohydrate (3)*	Diimidazolium suberate (4)*	Imidazolium sebacate (5) [7]
Formula	C <sub>9</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>14</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>18</sub> H <sub>31</sub> N <sub>2</sub> O <sub>6</sub>
Molecular weight	240.23	200.19	282.30	310.36	371.45
X-ray wavelength [Å]	1.54178	0.71073	0.71073	0.71073	1.54178
Crystal system	triclinic				
Space group	<i>P</i> -1				
<i>a</i> [Å]	7.2570(6)	8.420(2)	7.484(1)	7.842 (2)	8.825(1)
<i>b</i> [Å]	8.3020(10)	13.685(3)	8.934(2)	8.917 (2)	8.992(1)
<i>c</i> [Å]	9.3410(12)	17.068(3)	10.313	12.388 (2)	12.897(1)
$\alpha$ [°]	62.820(12)	90.62(3)	104.92(3)	88.74 (3)	95.22(1)
$\beta$ [°]	75.550(9)	103.45(3)	109.01(3)	73.59 (3)	92.91(1)
$\gamma$ [°]	88.070(8)	91.03(3)	106.55(3)	87.94 (3)	94.62(1)
Volume [Å <sup>3</sup> ]	482.68(9)	1912.2(7)	576.38(19)	830.4 (3)	1014.1(2)

\*Details of the crystal structures are deposited in CCDC(225442–225444) and will be published elsewhere.

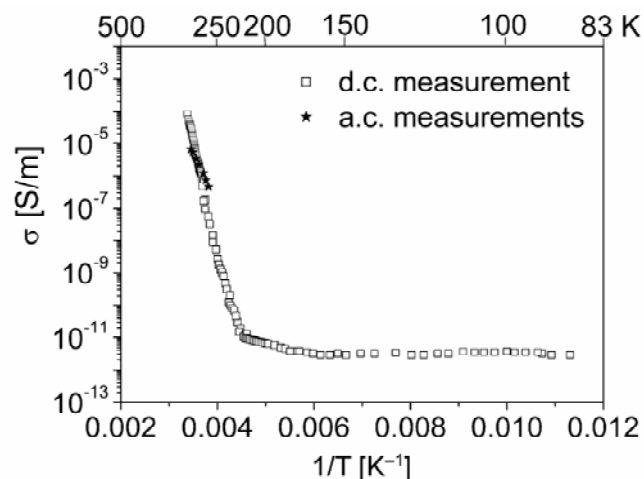
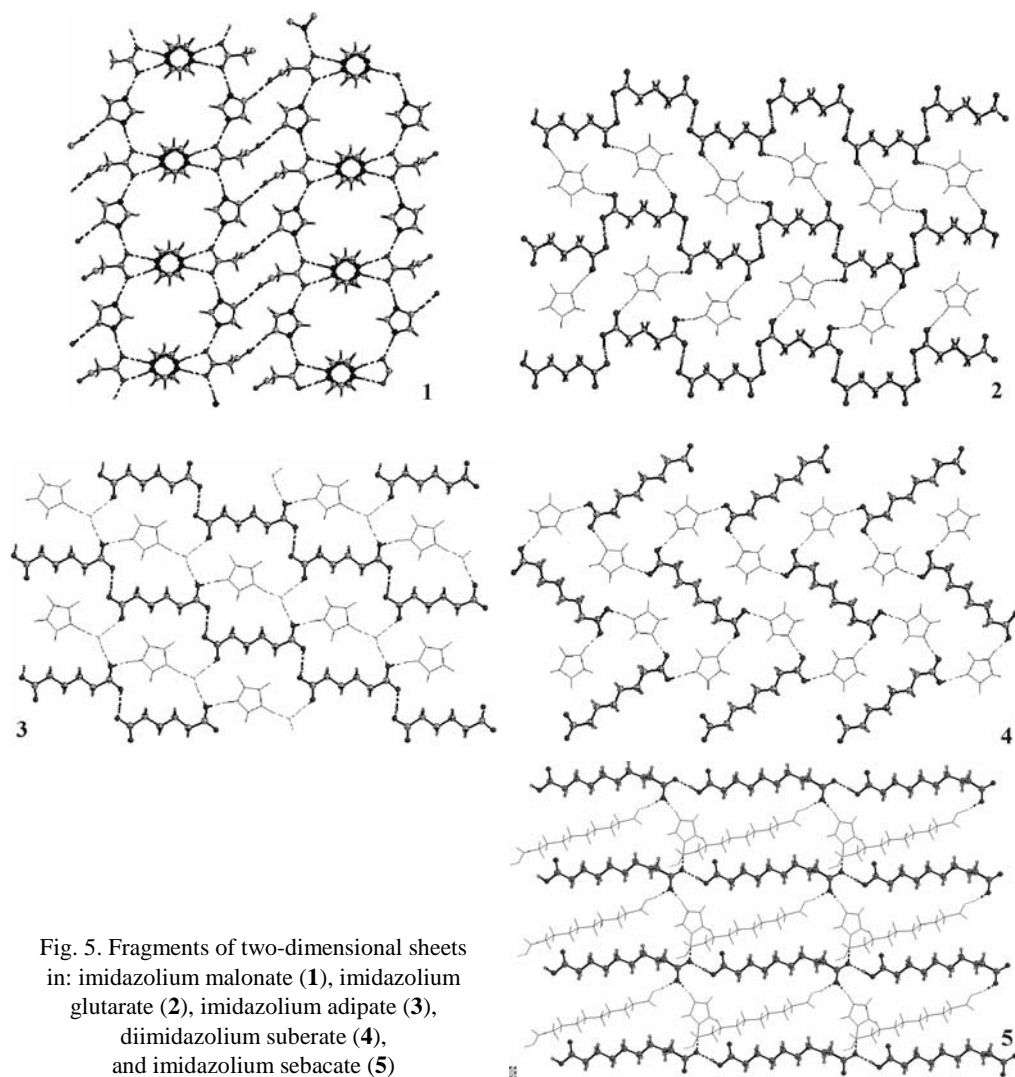


Fig. 4. Comparison of ac and dc conductivity measurements for imidazolium glutarate

bonded systems, the hydrophobic and hydrophilic parts are easily noticeable. The hydrophilic parts, with negative carboxylate anions and positively charged imidazolium cations, may serve as channels for proton transport. The lowest activation energy is noticed for imidazolium glutarate (0.7 eV). Such a low value can be connected to the specific stacking of imidazolium rings among acid molecules. This enables the formation of many possible N–H<sup>+</sup>⋯O interactions which play a crucial role in the conducting mechanism.



In imidazolium malonate, where a disordering of heterocyclic ring exists (Fig 5, 1), a similar value of the activation energy (0.75 eV) was noted. For imidazolium adipate, however, in which a water molecule is incorporated into the crystal lattice, the activation energy is higher (1.06 eV). H<sub>2</sub>O molecules form additional H-bonds between imidazole and acid moieties. On the other hand,  $E_a$  increases with the length of the methylene chain of the acid molecule. The highest activation energies are observed for diimidazolium suberate (4) (1.52 eV) and imidazolium sebacate (5) (1.68 eV). In the case of diimidazolium suberate, proton transfer is disabled by the unfavourable stacking of imidazolium cations among layers. In salt 5, the rotation of the imidazolium cation is limited by the presence of acid molecules, which bind adjacent layers.

It is known that the librations and rotations of imidazole molecules can play an important role in the mechanism of conductivity. The vibrations of imidazole molecules create virtual hydrogen bridges, which make the transportation of protons in the crystal easier.

#### 4. Conclusions

The presented results concerning conductivity and its correlation with crystal structures can be summarized as follows:

- At low temperatures all the investigated salts have low conductivities (of about  $10^{-12}$  S/m), typical of crystalline insulators.
- Starting at a certain temperature, the conductivities increase quickly according to the Arrhenius law to values in the range  $10^{-5}$ – $10^{-1}$  S/m just below the respective melting temperatures.
- As conductivity measurements were possible only for tablets (not for single crystals), there is some uncertainty regarding the influence of tablet preparation on the results. Nevertheless, all the investigated salts exhibit high conductivities in some temperature range before melting. The conductivity is comparable to that of superprotonic materials. The transition to the superionic state, which could be characterized e.g., by a low activation energy, is, however, not reached before melting.
- Knowledge of the crystal structures of imidazolium salts allows the conductivity mechanism to be proposed in relation to the arrangement of molecules in the solid state.
- The activation energy of proton conductivity can be discussed pointing the context of librations and rotations of the imidazole group. First, the activation energy strongly depends on the presence (among layers) of polar parts, which may serve as “channels” in the conducting mechanism. Second, the lengthening of acid molecules increases the activation energy.

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