

Short communication

Crystal structure and electrical conductivity of imidazolium succinate

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Abstract

Small single crystals of the imidazolium succinate were grown and their structure was re-examined using the X-ray diffraction method and a probable protonic conduction mechanism has been proposed. The electric conductivity of the powdered tablets was measured using the impedance spectroscopy method. The range of obtained values of conductivity as well as the activation energy (0.65 eV) of the imidazolium succinate is close to these of imidazolium malonate and imidazolium glutarate investigated previously [K. Pogorzelec-Glaser, J. Garbarczyk, Cz. Pawlaczyk, E. Markiewicz, *Materials Science Poland* 24 (2006) 245–253]. Metastable and virtual positions for proton transfer were indicated by means of calculations of the atomic displacement factors and the probability density function.

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1. Introduction

Imidazole as a nitrogen heterocycle is known to exhibit interesting special biological properties. The molecule can serve as a proton transfer agent in living systems [1]. Because of its specific molecular structure it is able to act as a weak acid and as a strong base. In search of anhydrous materials which can be applied as solid electrolytes in fuel cells we have recently investigated structure and electrical conductivity of five new imidazolium salts of dicarboxylic acids: imidazolium malonate, imidazolium glutarate, imidazolium adipate monohydrate, diimidazolium suberate, and imidazolium sebacate [2,3]. There were salts having 1, 3, 4, 6 and 8 CH₂ molecules in the acid's chain, respectively. The electrical conductivity of the salts behaves qualitatively similar. At low temperatures they display low conductivity (of about 10⁻¹² Sm⁻¹), typical for crystalline insulators. Starting at a certain temperature (between 230 and 290 K for various salts), the conductivity of the salts increases quickly according to the Arrhenius law up to values in the range 10⁻⁵ to 10⁻¹ Sm⁻¹ just below the respective melting temperatures (between 368 and 401 K) [2]. The activation energy increases with the number of the CH₂ molecules in the acid chain [2].

Continuing our study recently we have grown single crystals of the imidazolium succinate, having 2 CH₂ groups in the acid's chain. The crystals structure of the imidazolium succinate was previously solved by J.C. MacDonald et al. [4]. In this paper, we present the results of the redetermination of the crystal structure at 293–330 K with a discussion of the motion of imidazole molecules. The aim of our study was to find the possible diffusion paths of the protons in the crystal lattice and to refer the structural data to measurements of the electrical conductivity of powdered samples.

2. Experimental

2.1. Synthesis and crystallization

Imidazole and dicarboxylic acid (starting materials, approximately 99% pure, were obtained from Sigma–Aldrich and Fluka) was separately dissolved in anhydrous ethyl acetate and the mixtures were added together. Reaction product as a white precipitate was separated and washed with anhydrous ethyl acetate. Crystallisation of the salt was carried out from acetone solution of the precipitate.

2.2. Conductivity measurements

Because of the small sizes of the obtained crystals the conductivity measurements were carried out on powder samples

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in form of discs of 13 mm in diameter and 2 mm thick. They were prepared by pressing under $p = 50$ MPa during $t = 20$ min at room temperature. The surfaces of the samples were covered with silver paste electrodes. The real and imaginary parts of the electrical impedance were measured in the frequency range 100 Hz to 13 MHz by means of a computer-controlled HP-4192 A impedance meter. The temperature of the sample was stabilized using a CF 1204 Oxford Instruments Cryostat, equipped with an ITC4 temperature controller.

2.3. X-ray measurements

Single crystal X-ray diffraction measurement was performed using X-ray four-circle Xcalibur Diffractometer (Oxford Diffraction Company) with CCD area detector at 298–330 K. Graphite monochromated Mo $K\alpha$ radiation was generated at 50 kV and 25 mA. The crystal structure of salt was redetermined using SHELXL-97 and JANA2000 programs [5,6]. To analyze the anharmonic motion of atoms the calculations of the anharmonic probability density functions (pdfs) were used [7]. The CIF files with the crystal data at 298–330 K have been sent to a deposit in CSD base.

3. Results and discussion

3.1. Crystal structure analysis

The redetermination of crystal structure of imidazolium succinate confirmed the previous results obtained by Mac Donald [4]. Details of the refinements are presented in the Table 1.

The crystal structure belongs to the triclinic system with the $P-1$ space group. The unit cell of imidazolium succinate contains one crystallographically independent molecule of imidazolium

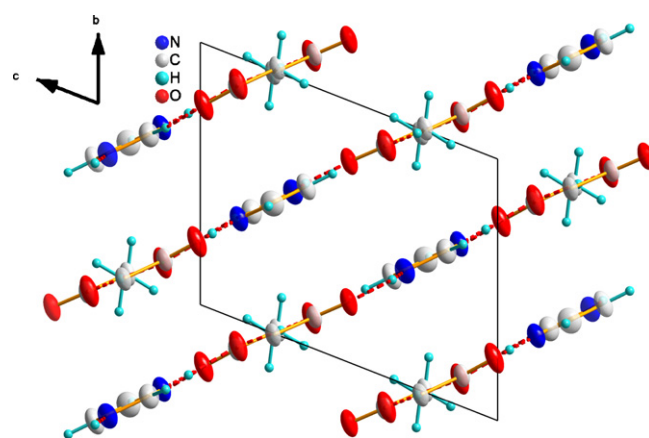


Fig. 1. Projection of the crystal structure along a -axis.

and one of succinic acid. Fig. 1 shows the projection of the crystal structure along the a -axis. The imidazolium cations and succinate anions form layers parallel to the $(0\ 1\ -1)$ plane. The distance between the layers is about 3.385 Å. Dihedral angle between a plane of imidazolium cation and a plane of succinate anion is 3.875°. Displacement factors for imidazolium rings among the layers are two times larger comparing to the perpendicular direction (see Fig. 2). In the layers, the chains of the acid's molecules are bonded by strong hydrogen bonds $O-H \cdots O$ (2.478 Å). Also the succinate anions create the second type $N-H \cdots O$ hydrogen bonds with the imidazolium cations. In the imidazolium succinate all mentioned carboxyl groups adopt *anti-anti* conformation.

Table 2 presents the lengths of chosen hydrogen bonds in analyzed salt (“D” stands for donor and “A” for acceptor).

The diffusion of the proton in ionic conductors corresponds to low transition barriers among following positions in crys-

Table 1
Crystal data and details of the structure refinement at 298–330 K (JANA2000)

Identification code	IMD-succinate	
Empirical formula	$C_7 H_{10} N_2 O_4$	
Formula weight	186.2	
Temperature K	293	330
Wavelength	0.71073 Å	
Crystal system, space group	TRICLINIC, $P-1$	
Unit cell dimensions	$a = 6.5766$ Å $\alpha = 67.9531^\circ$ $b = 7.4109$ Å $\beta = 73.9152^\circ$ $c = 9.6479$ Å $\gamma = 81.4088^\circ$	$a = 6.6044$ Å $\alpha = 67.594^\circ$ $b = 7.5084$ Å $\beta = 73.9311^\circ$ $c = 9.7053$ Å $\gamma = 81.4614^\circ$
Volume	418.234 Å ³	427.0536 Å ³
Z, calculated density Mgm^{-3}	2, 1.478	2, 1.4473
Absorption coefficient	0.122 mm^{-1}	
$F(000)$	196	
Crystal size	0.31 mm \times 0.25 mm \times 0.22 mm	0.29 mm \times 0.24 mm \times 0.21 mm
Theta range for data collection	3.90–28.14°	2.94–28.11°
Limiting indices	$-7 \leq h \leq 8$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$	$-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-10 \leq l \leq 12$
Reflections collected/unique	4234/4234 [$R(int)$ 0.0104]	4288/4288 [$R(int)$ 0.0214]
Completeness to $\theta = 28.14^\circ$	95%	95%
Data/restraints/parameters	2828/0/248	2020/0/248
Goodness-of-fit on F^2	1.237	1.37
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0407$, $wR2 = 0.0308$	$R1 = 0.0365$, $wR2 = 0.0221$
R indices (all data)	$R1 = 0.0593$, $wR2 = 0.309$	$R1 = 0.0911$, $wR2 = 0.0233$
Extinction coefficient	0.00001(17)	0.00002(17)

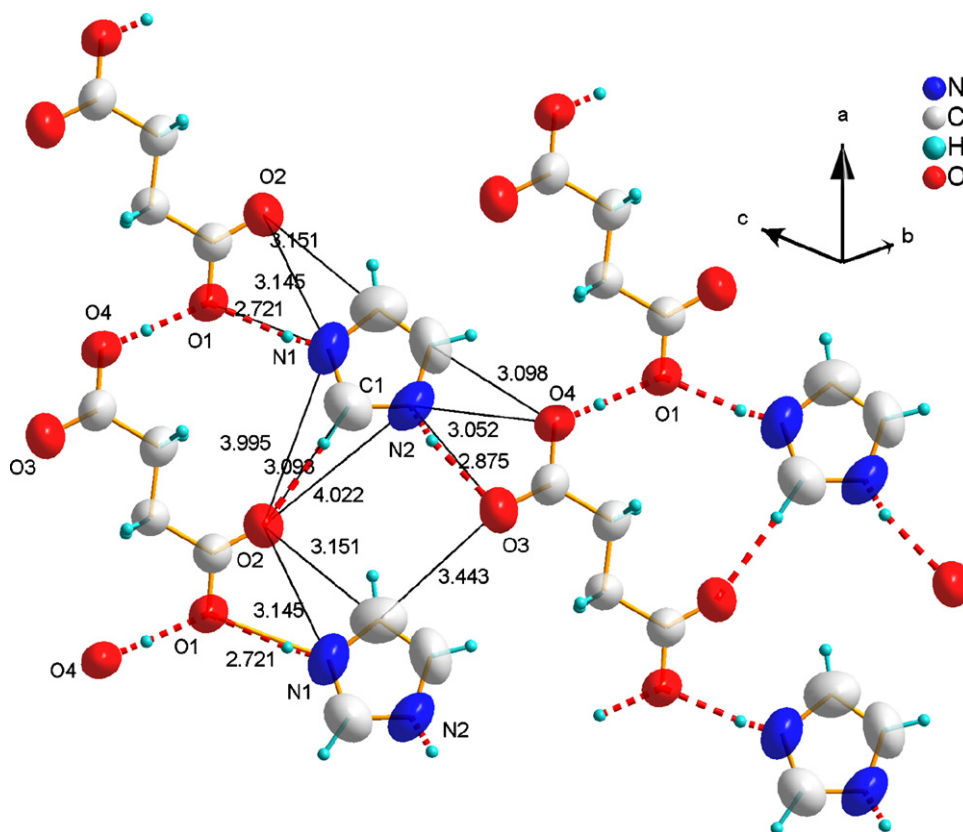


Fig. 2. Projection of the single layer parallel to $01\bar{1}$ plane. Black thin lines show an arrangement of the virtual hydrogen bonds between the imidazolium cations and succinate anions. Ellipsoids present the magnitude of the displacement factors, which correspond to the vibration of atoms.

tal structure. The probability density functions (pdfs) close by the split-atom models well describes disordered crystal structures connected with the migration of the proton. Pdfs gives information about the values of the potential barriers.

The displacements factors of the atoms of the imidazole molecules show that the motion significantly increases with the increasing temperature. To investigate this effect we refined of crystal structure using the anharmonic Gram–Charlier model [8]. The parameters of displacements factors of C and N atoms for imidazole molecule were refined using third order anharmonic approximation.

Table 2
Lengths of hydrogen bonds at 298–330 K (SHELXL-97)^a

D–H	H...A	D...A	<(DHA)
At 298 K			
0.913 (7)	1.812 (7)	2.7205 (10)	172.9 (7) N1–H1...O1
0.858 (7)	2.034 (7)	2.8746 (10)	166.4 (6) N2–H2...O3_\$1
0.858 (7)	2.618 (6)	3.0519 (11)	112.5 (5) N2–H2...O4_\$1
1.038 (6)	1.442 (6)	2.4804 (10)	178.3 (7) O4–H3...O1_\$1
At 330 K			
0.937 (6)	1.809 (6)	2.7435 (10)	174.9 (6) N1–H1...O1
0.901 (7)	2.010 (6)	2.87950 (10)	166.9 (5) N2–H2...O3_\$1
0.901 (7)	2.616 (5)	3.0746 (12)	112.4 (4) N2–H2...O4_\$1
1.068 (6)	1.415 (5)	2.4826 (10)	178.0 (7) O4–H3...O1_\$1

^a Symmetry transformation used to generate equivalent atoms: \$1 $x-1, y+1, z-1$.

Fig. 3(a and b) represents, the joint probability distribution map calculated at 298–330 K. It indicates on the strong libration of imidazole molecule with respect to its normal plane.

The decreasing potential barriers of the protons from 60 meV at 298 K to 40 meV at 330 K confirm their migration ability.

Because the crystal structure of imidazolium succinate belongs to the layer type structure it shows a strong anisotropy of the properties, particularly of the electric conductivity. The two dimensional network of the hydrogen bonds in the layer can constitute the conductivity paths for protons as is proposed in Fig. 4.

As it is seen in Fig. 2 the imidazole cations exhibit very large motions in the plane $01\bar{1}$. The motions lead to fast diffusion of the protons from one to next metastable positions (see Fig. 2). The preliminary refinement of the crystal structure with the anharmonic displacement parameters for the C and N atoms of the imidazolium cation and the calculation of a probability density functions indicated that the path with the lower potential barriers for the diffusion of proton is along $[100]$ axis. The higher barriers are noticeable along the $[14\bar{9}]$ direction (see Fig. 4).

3.2. Ionic conductivity

Electrical conductivity measurements were carried out by means of impedance spectroscopy for tablets made of the powdered imidazolium succinate single crystals as described above.

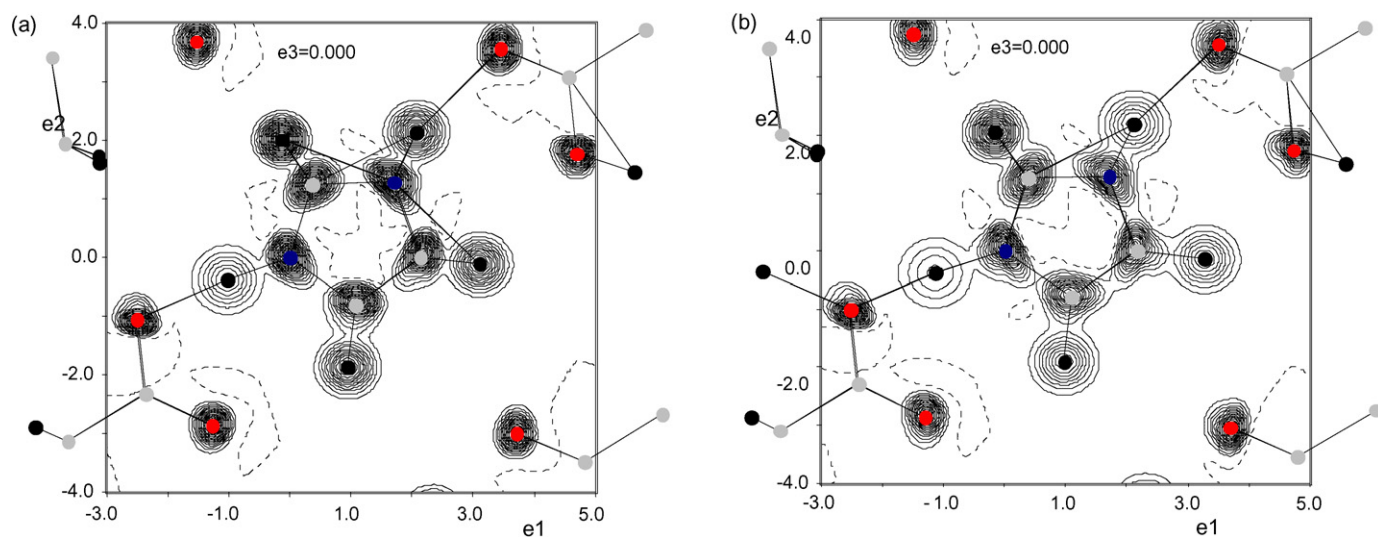


Fig. 3. Joint pdfs maps for imidazole molecule (a) at 298 K and (b) at 330 K.

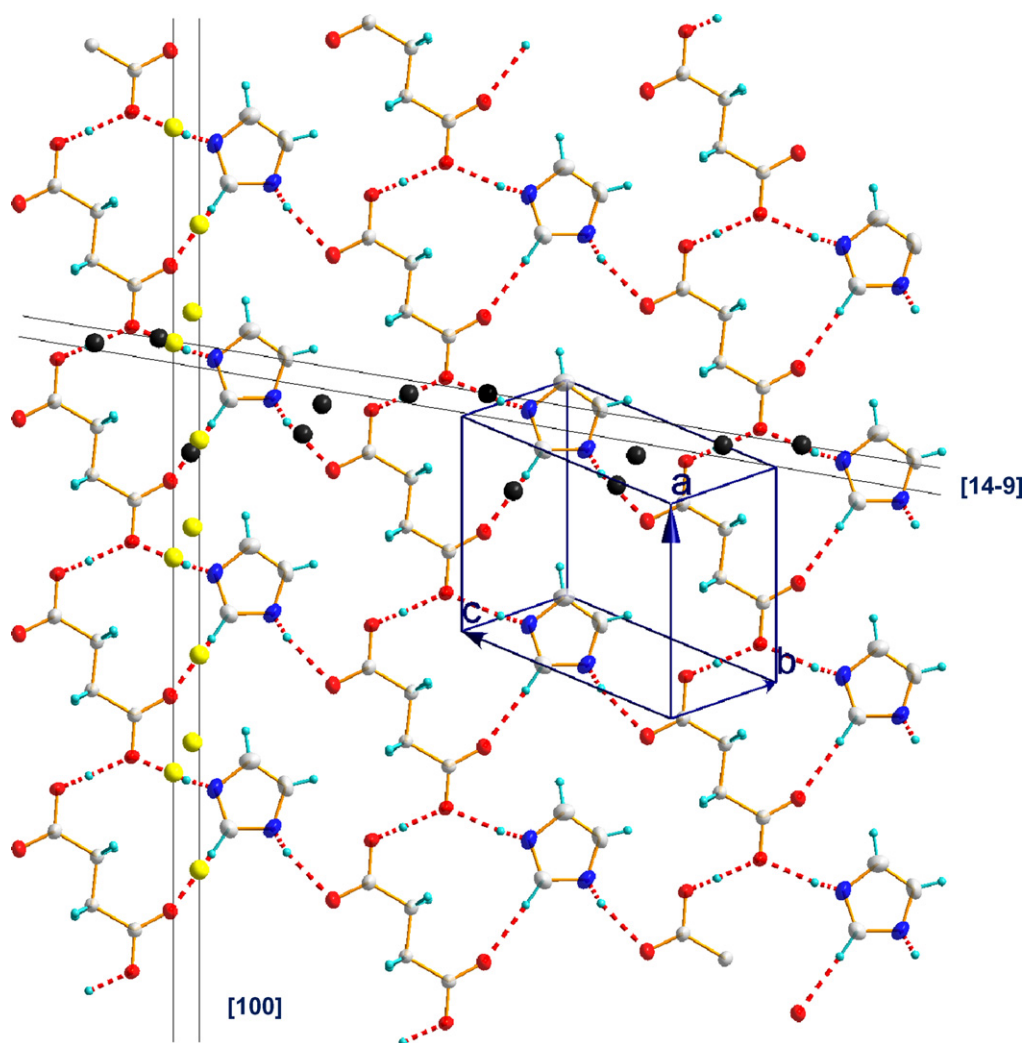


Fig. 4. Illustration of the suggested proton paths in the layer (yellow point—metastable position of the proton along $[1\ 0\ 0]$ axis, black circle—virtual position along $[14\ -9]$ direction).

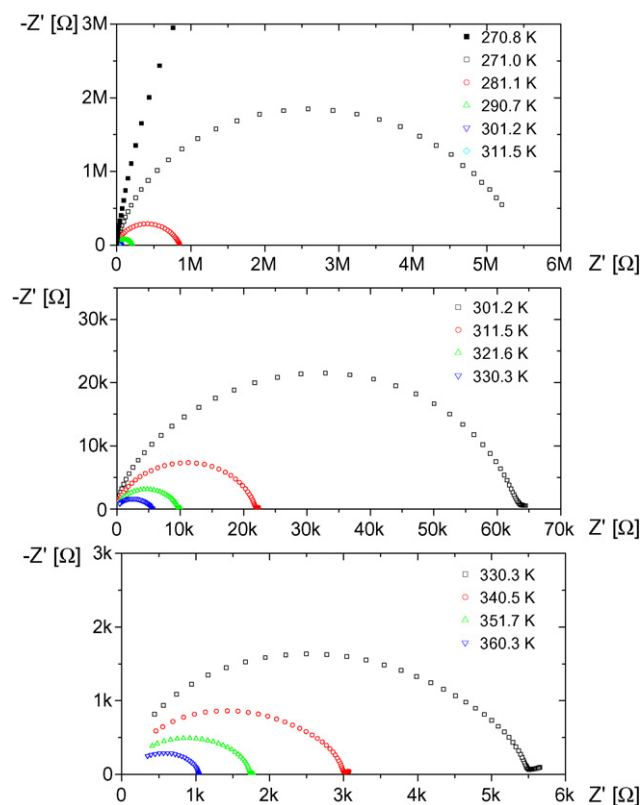


Fig. 5. Argand diagram for a powdered imidazolium succinate sample.

Unfortunately, such measurements cannot be the evidence of the expected conductivity anisotropy.

The dependence of the imaginary part of impedance Z'' on the real part Z' (Argand diagram) is shown in Fig. 5(a–c). The experimental points compose flattened semicircles tending to the origin of the $-Z''$, Z' coordinate system. It means that the investigated samples were not homogenous with respect to their resistance R and capacity C . The sample cannot be represented by only one parallel equivalent circuit RC with a single time constant RC . It is rather composed of areas characterized by close but not the same time constant. This conclusion seems to be plausible for the powder sample composed of many single crystals pressed together.

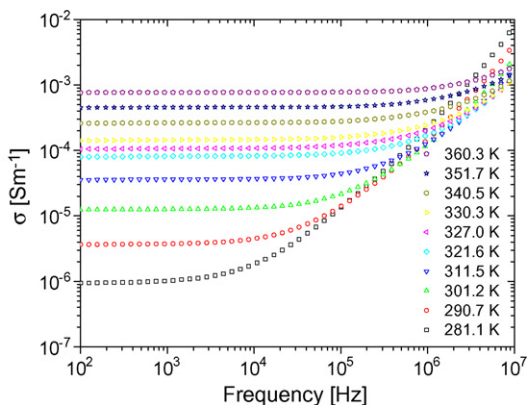


Fig. 6. Frequency dependence of ac conductivity (σ_{ac}) for imidazolium succinate.

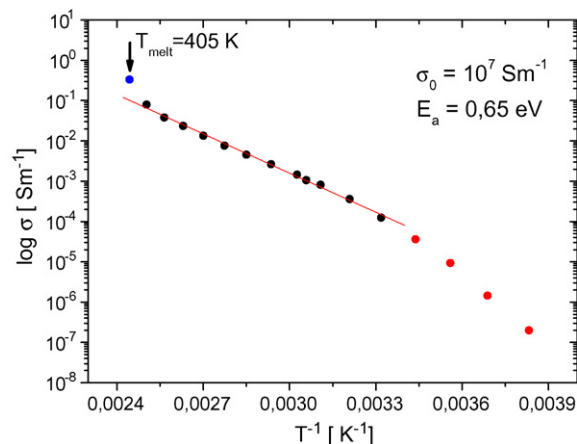


Fig. 7. Arrhenius plot for imidazolium succinate.

Table 3

Activation energies of imidazolium succinate and salts investigated previously [2,9]

Compound	Activation energy (eV)
Imidazolium malonate	0.75
Imidazolium succinate	0.65
Imidazolium glutarate	0.70
Imidazolium adipate	1.06
Diimidazolium suberate	1.52
Imidazolium sebacate	1.68

Fig. 6 shows the frequency dependence of ac conductivity (σ_{ac}) for imidazolium succinate. From the low frequency plateau of each $\sigma_{ac}(f)$ curve one can evaluate the dc conductivity σ_{dc} for a given temperature. The Arrhenius plot, $\sigma_{dc}(1/T)$, obtained from the ac results for imidazolium succinate is displayed in Fig. 7. The Arrhenius law:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right) \quad (1)$$

where E_a denotes the activation energy, σ_0 denotes pre-exponential factor and k denotes the Boltzmann constant is fulfilled in the temperature range 300–400 K (near to melting point) and the activation energy calculated for this part of the plot amounts 0.65 eV. The observed deviation from the Arrhenius behaviour at highest temperatures is caused by the initial melting of the sample. At low temperatures the resistivity of the sample is very high (much above $10^7 \Omega$) and cannot be estimated with sufficient accuracy.

The calculated values of activation energy for the previously measured five imidazolium salts [2,9] as well as for imidazolium succinate are summarized in Table 3. The activation energy was found to be close to that obtained for imidazolium malonate and imidazolium glutarate.

4. Conclusions

The imidazole molecules, like other heterocycles rings, are known to condense in crystalline structures held together by

hydrogen bond networks. Munch et al. [10] have shown that in such networks the excess protons can diffuse like protons in water due to the Grotthus mechanism. The existence of the Grotthus mechanism has been established experimentally also for imidazolium crystal [10]. In our case, for imidazolium dicarboxylic salts, similar mechanism of the transport of the protons can be proposed. The model of the pathways of the proton transfer for imidazolium succinate presented in Fig. 4 has been suggested taking into account the displacement factor of nitrogen and oxygen atoms and the length of the possible hydrogen bonds between imidazole and acid groups in the layer. It should be noticed that the number of the possible, metastable proton positions in the layer (black points in Fig. 4) is larger than those statically occupied. The model of the proton transfer in imidazolium succinate suggests a strong anisotropy of the ionic conductivity which can be experimentally confirmed by measurements performed on single crystals only. Our measurements made on powdered samples have shown that the protonic conductivity of the salt really increases rapidly in the whole investigated temperature range. Near the melting point the con-

ductivity reaches the value (10^{-1} Sm^{-1}) which makes the salt interesting for applications as solid electrolyte.

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