



The proton conductivity in benzimidazolium azelate under moderate pressure



T. Masłowski^{a,*}, A. Drzewiński^a, P. Ławniczak^b, M. Zdanowska-Frączek^b, J. Ulner^c

^a Institute of Physics, University of Zielona Góra, ul. Prof. Z. Szafrana 4a, 65-516 Zielona Góra, Poland

^b Institute of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60-179 Poznań, Poland

^c Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-422 Wrocław, Poland

ARTICLE INFO

Article history:

Received 8 December 2014

Received in revised form 4 May 2015

Accepted 5 June 2015

Available online 19 June 2015

Keywords:

Anhydrous proton conductor

Heterocyclic-based compounds

High pressure

Kinetic Monte Carlo

ABSTRACT

The kinetic Monte Carlo method is applied to examine effects of hydrostatic pressure on the benzimidazolium azelate (BenAze) proton conductivity. Following the experimental indications the recently proposed model has been modified to simulate the transport phenomena under moderate pressure, resulting in a very good agreement between numerical and experimental results. We demonstrate that the pressure-induced changes in the proton conductivity can be attributed to solely two parameters: the length of the hydrogen bond and the amplitude of lattice vibrations while other processes play a minor role. Furthermore, in high-pressure regime we anticipate the crossover from the increasing to decreasing temperature dependence of the proton conductivity arising from the changes in the hydrogen-bond activation barrier with increased pressure.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Proton conductivity is a very interesting transport phenomenon involved in the long-range charge transfer mechanism. The recent great interest in proton transfer unassisted by water comes from the search for fuel cells operating above the boiling point of water (373 K) but below extremely high temperatures typical for solid oxides. One possibility is to create a proton conductor on the basis of heterocyclic compounds [1,2] that display many characteristics to water: they are amphoteric, undergo autoprotolysis and possess the ability to form hydrogen bonds (H-bonds) and most importantly, they have substantially higher melting points (e.g., benzimidazole—447 K). Based on these properties various proton conductors, both the polymer [3–7] and crystalline [8,9] can be created. In recent years we have focused on the dicarboxylic acid salts family. Such crystalline anhydrous proton conductors are organic molecules formed with heterocyclic nitrogen-containing organic chains of imidazole, triazole or benzimidazole. These compounds have a number of structural similarities: the chains which are formed from acids and heterocyclic molecules are linked by H-bonds while the layers are stabilized by the weak electrostatic interaction. In general, the proton conductivity increases with temperature according to the Arrhenius law indicating the dominant character of the Grotthuss mechanism [10,11].

Proton conductivity of anhydrous heterocyclic-based materials is a complex process affected by many external factors, e.g. temperature

and pressure. An external pressure influences the length of the H-bond and modifies the mobility of structural elements involved in the process. In the literature, the effect of pressure on proton conductivity is analyzed mainly for materials exhibiting a phase transition to the highly conductive phase (superprotonic), for example, $\text{C}_6\text{H}_5\text{SO}_4$ [12] or $[(\text{NH}_4)_x\text{Rb}_{1-x}]_3\text{H}(\text{SO}_4)_2$ [13,14]. The application of the hydrostatic pressure causes an increase in the thermal stability of the superprotonic phase [13]. This is mainly due to an increase in the melting point, while the phase transition temperature varies slightly with an applied pressure. The similarity of the p - T phase diagrams of compounds belonging to the $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$ class of proton conducting crystals (where $M = \text{K}, \text{Cs}, \text{Rb}, \text{NH}_4$ and $X = \text{S}, \text{Se}$) also suggests the possibility of inducing the superprotonic phase even at the absence of the normal atmospheric pressure conditions [15,16].

The electric properties and molecular dynamics of BenAze at ambient pressure have been studied experimentally in [17,18]. The studies revealed that the temperature dependence of the proton conductivity can be fitted to the Arrhenius law and is well described by the Grotthuss-type diffusion mechanism. Moreover, a detailed description of the proton migration path was proposed [18]. The proton conductivity studies performed at different thermodynamic conditions [17–20] disclosed that BenAze is extremely sensitive to external pressure. In particular, the proton conductivity decreases with increasing pressure and the significant change in the shape of the conductivity curve is observed from linear (the Arrhenius-type behavior) to nonlinear one. However, a scaling procedure between the ac conductivity, dc conductivity, current frequency and pressure (proposed by Sommerfeld [21]) leading to one master curve for various temperatures at ambient pressure is well

* Corresponding author.

E-mail address: T.Maslowski@if.uz.zgora.pl (T. Masłowski).

preserved also for different pressures at a fixed temperature [17]. This indicates the presence of the same mechanism responsible for proton conductivity at various thermodynamic conditions.

Therefore, we have attempted to support the experimental results observed at elevated pressures by microscopic model simulations. The theoretical model describing the proton transport based on a chain model consisting of rigid rods in accordance with the Grotthuss mechanism has been presented recently [22]. The model is based on the kinetic Monte Carlo (KMC) approach adequate to characteristic time scales of the proton conduction [23]. In the KMC method a sequence of discrete transitions (the Markovian process) from one energy minimum state to another is described by transition rates that depend on the energy barrier between states. The selection of which state is next visited and after which amount of time the corresponding transition occurs follows the probabilities prescribed by the master equation [24].

In Ref. [22] we have proposed the model where benzimidazole molecules form a long chain connected to one another by hydrogen bonding and all necessary transitions are known. This resulted in a very good agreement between the numerical results and experimental measurements. However, in the present study, we investigate a much more complex compound made of infinite azelaic acid anion chains connected with benzimidazolium cations by various H-bonds. We will argue that in the present case the recognition of the crucial role of the proton hopping through the strongest hydrogen bond is key. Then we can modify our rod model [22] to reproduce the essential features of the BenAze conductivity, in particular the influence of hydrostatic pressure. The presence of pressure, on the one hand, increases the complexity of the issue, but on the other allows for the validation of the model assumptions because they are pressure sensitive. Furthermore, some practical conclusions are drawn for the high pressure range that have not yet been studied experimentally.

The paper is organized as follows: in Section 2 we present the microscopic model to study the effects of moderate hydrostatic pressure in BenAze. In Section 3 the simulation results are presented and discussed. Finally Section 4 concludes our paper, and summarizes the main findings.

2. The proton conductivity model of BenAze

Although BenAze is regarded as a poor proton conductor ($< 10^{-4}$ S/m) it is a good candidate for an investigation as its crystal structure is known. The characteristic structural features of the BenAze crystal are parallel two-dimensional layers. The proton transport within these planes occurs along a one-dimensional path [18] comprising hydrogen bridges [17]. The reliable modeling of diffusion process for BenAze in the KMC approach requires the precise experimental data that would enable us to extract a large number of parameters describing the individual subprocesses contributing to the proton transport. As such experiments are still missing, we may use only the structure data, which is far not enough. Therefore, we have decided to employ another strategy. Crucial is that the net transport of protons is similar to the pipeline transport and the entire conduction is limited by the narrowest place, called a bottleneck. In agreement with Ref. [18] we assume that the bottleneck's role is played by the N–H \cdots N bond between benzimidazoles, see Fig. 1. Because it is the strongest H-bond then it also exhibits the lowest transfer in the entire path. Thus, our idea is to focus on this bond and attempt to model its features in detail.

To overcome the problem of remaining elements of the transfer path, we treat all other processes (benzimidazole flips, the remaining tunnelings and trans-gauche motion of azelate acid chains) as a result of the “black box” activity. Each proton arrangement at the “black box” ends corresponds to a local-minimum free energy configuration which is essential for the KMC algorithm. The basic function of the “black box”, as for the rotation in the standard Grotthuss mechanism, is to supply a proton to the strongest N–H \cdots N bond with the frequency ν_R . It is the only effective parameter introduced to model the behavior of the “black box”. A proton can change the localization from one end of the “black box” to another. It may also happen that two protons at opposite ends of the same “black box” exchange positions and consequently the configuration remains unchanged. The same can also occur when the “black box” without protons at the ends is drawn during the KMC sampling which means that there is no proton transmission at all. In order to calculate the proton current we count protons crossing a

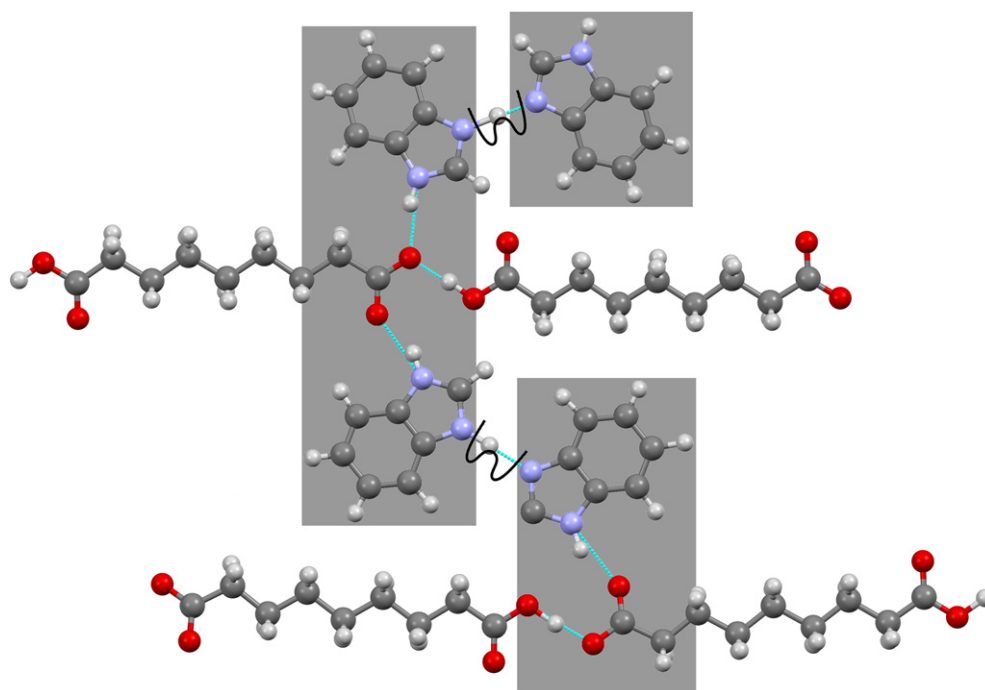


Fig. 1. Schematic illustration of the proton conduction path in BenAze. Shaded rectangles represent the “black boxes” while the double-well curves between them correspond to the “bottleneck” H-bonds.

Download English Version:

<https://daneshyari.com/en/article/1295704>

Download Persian Version:

<https://daneshyari.com/article/1295704>

[Daneshyari.com](https://daneshyari.com)