

# Numerical modeling of the heterocycle intercalated proton-conducting polymers at various mole ratios



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## ABSTRACT

The kinetic Monte Carlo simulations are employed to study the proton conductivity for anhydrous heterocyclic based polymers. The proton transport is based on a two-step process called the Grotthuss mechanism. In the referring system the proton concentration depends on the relative molar ratio,  $x$ , of the benzimidazole and the polystyrene sulfonic acid. Available experimental data with contrasting behavior are fitted and interpreted in terms of our microscopic model. Moreover, it has been shown that the current behavior similar to the Vogel–Tamman–Fulcher law can be reproduced with high precision on the basis of the Grotthuss mechanism.

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## 1. Introduction

The microscopic modeling of proton transport is one of the long-standing problems in many areas of science ranging from conversion of chemical energy into electrical one to various biological systems [1, 2]. Ice and water became the first hydrogen-bonding systems for which the microscopic description of proton defect transport has been provided in great detail [3]. However, as there are several advantages of fuel cells operating above the boiling temperature of water [4], recently the polymer systems which conduct protons in the absence of any water have become the subject of intensive research. Unfortunately, the proton conductivity of conventional polymer membranes under anhydrous condition is usually very low. Therefore, the promising strategy for the synthesis of new materials was the doping of a high boiling proton solvent into a polymer matrix. Then the proton transport occurs almost entirely through the Grotthuss mechanism, a two-stage mechanism [5,6], consisting of thermally induced reorientation and proton tunneling in hydrogen bonds (H-bonds).

As is well known, both chemical and physical properties of a polymer material may change with substitution. So to get polymer electrolytes the polymer matrix (e.g., polystyrene, polyacrylate, polysiloxane) is doped by amphoteric nitrogen-based heterocycles (e.g., imidazole, triazole, benzimidazole) at various mole ratios [7–9]. As a result the heterocycles may be covalently tethered to a suitable polymer and

linked by the N–H–N hydrogen bridges providing a migration path for excess of protons emerging from the dissociation of the acid functions.

For many heterocyclic based polymer proton conductors the temperature dependence of dc conductivity follows at low doping ratios  $x \leq 1.0$  ( $x$  is the number of moles of heterocycle per polymer repeat unit containing the acidic group) the simple Arrhenius law

$$\sigma = \sigma_0 \exp(E_a/k_B T), \quad (1)$$

where  $E_a$  is the activation energy for proton migration,  $k_B$  is Boltzmann's constant and  $\sigma_0$  corresponds to carrier proton number. But what is intriguing, at a high doping the temperature-dependent conductivity seems to follow the Vogel–Tamman–Fulcher (VTF) law [10–12]

$$\sigma = \sigma_0 \exp(E_a/k_B(T-T_0)) \quad (2)$$

typically associated with a viscous material whose conductivity is driven by the segmental motions above the glass transition temperature. The parameter  $T_0$  corresponds to the temperature where the free volume disappears. Moreover, for these compounds the crossover driven by the molar ratio is accompanied by an abrupt increase in proton conductivity for  $1 < x < 1.5$ .

To address this controversy, we have evaluated the experimental data in the wide range of doping ratio [10] employing the model [13] based on the kinetic Monte Carlo (KMC) simulations [14–17] which we describe briefly here. The proton conduction process of the immobilized heterocycles can be considered as a cooperative one involving both molecular motions prior to the proton exchange (by

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the 180° flip) and migration along the H-bond chain. It can be well modeled by the one-dimensional system of rods each of which has only two positions where the rod ends can be occupied by protons. The key point is to know a priori all transition rates from every configuration to any other allowed one [16]. When it is satisfied the KMC method gives the answer to the question of how long the system remains in the same configuration and to what configuration it will evolve [14]. Herein, the rotations, as a sub-process, are treated as a thermally activated process satisfying the Arrhenius law [Eq. (1)] with the activation energy,  $E_a$ , given by

$$E_a = \max(0, V_{\text{act}} + |e|Kb) , \quad (3)$$

where  $V_{\text{act}}$  is the activation energy for rotation in the vanishing electric field,  $e$ —the value of the elementary charge,  $K$ —the external electric field strength, and  $b$ —the size of the rod. The prefactor  $\sigma_0$  (in this case called the frequency of rotation  $\nu_R^0$ ) is calculated by solving the Schrödinger equation for the one-dimensional quantum rotor (see [13]).

The migration of a proton from one rod to another represents the hopping between the minima of the H-bond potential. Hopping is defined as the thermally assisted tunneling which is an extension of the purely classical Arrhenius behavior. We approximate the H-bond potential by the fuzzy Morse potentials originating in rod ends as they represent anionic groups between which the H-bonds are created.

$$V_a(z) = \frac{1}{2a} \int_{-a}^a \left[ V_{\text{Morse}} \left( \frac{d}{2} - z + y \right) + V_{\text{Morse}} \left( z - y - \frac{d}{2} \right) \right] dy, \quad (4)$$

$$V_{\text{Morse}}(z) = g \left[ \exp \left( -\frac{2z}{w} \right) - 2 \exp \left( -\frac{z}{w} \right) \right]. \quad (5)$$

$V_a(z)$  is the double well potential and the parameter  $a$  controls the dispersion in the position of the anionic groups forming the H-bond. Thus, it represents the thermal lattice vibrations. The Morse potential parameters  $g$  and  $w$  are adjusted to get the distance between the minima of the double well potential  $V_a$  equal to  $\Delta z$  together with the height of the barrier equal to  $h$ .  $V_a(z)$  is used to get quantum analog of the Arrhenius law [18]. In this case the prefactor  $\sigma_0$ , called the frequency of tunneling, is denoted by  $\nu_T^0$ . More details about the model can be found in our previous paper [13].

This paper is organized as follows: in Section 2 the proton concentration with respect to the molar ratio is determined. In Section 3 the referring experimental system is presented as well as the simulation results are discussed. Section 4 concludes our paper summarizing the main outcomes.

## 2. Molar ratio influence on the proton concentration

The blends of polymer and heterocycles are prepared for various  $x$  where the results are transparent and homogeneous thin films. The larger ratio  $x$  the lower the average distance between the heterocycles, which in turn significantly modifies the character of the H-bond potential. As the amphoteric nitrogen-based heterocycles demonstrate the presence of both protonated and non-protonated nitrogen atoms they can act as donors and acceptors in proton-transfer reactions. Therefore, the change of  $x$  affects the concentration of protons,  $c$ , on the heterocycle path: a parameter crucial for the proton conductivity ([13], see the inset in Fig. 1).

In order to determine the function  $c(x)$  we have performed the numerical simulations considering two types of particles,  $A$  and  $B$  with the relative ratio  $x$ , randomly distributed at sites on a simple cubic lattice. When the adjacent sites are occupied by  $A$  and  $B$ , they may form a pair (one particle can be paired only once). The concentration

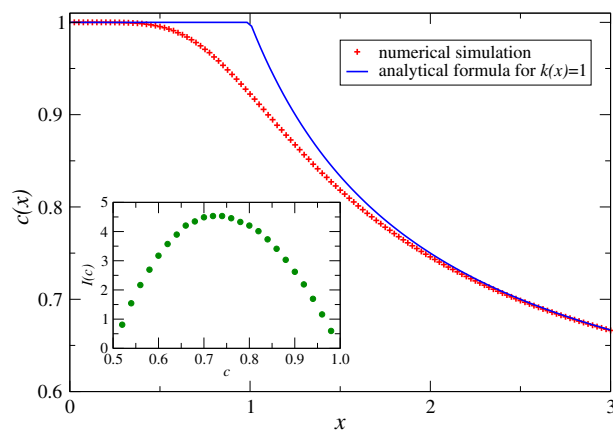


Fig. 1. The proton concentration as the function of the molar ratio, the result for the  $125 \times 125 \times 125$  system. The solid line represents the asymptotic behavior. Inset: The current dependence on the proton concentration [13].

$c(x)$  may be expressed in terms of the function  $k(x)$  describing the probability that  $A$  is attached to  $B$ :

$$c(x) = \frac{1}{2} [1 + k(x)]. \quad (6)$$

The function  $k(x)$  is calculated as the ratio of paired  $A$  particles to the number of all  $A$  particles. Simulations were performed for system sizes  $75 \times 75 \times 75$ ,  $100 \times 100 \times 100$  and  $125 \times 125 \times 125$ . The function  $c(x)$  converges quickly with the system size, providing that the differences between the results for the two largest systems are indistinguishable.

If a simplifying assumption is considered that  $A$  is always attached to  $B$ , provided that there is a free  $B$  particle then simple analytical expressions for asymptotes can be derived:  $c(x) = 1$  when  $x$  goes to zero and  $c(x) = (x + 1)/(2x)$  when  $x$  is large (see Fig. 1).

In our case  $A$  represents a heterocycle while  $B$  a polymer unit, and pairing should be understood as forming the anionic group by deprotonation of the acidic group by doping with the heterocycle, e.g.,  $\text{BnIm} + \text{SO}_3\text{H} \rightarrow \text{BnImH}^+ + \text{SO}_3^-$  (the benzimidazole is abbreviated to BnIm). In this way some heterocycles are protonated at “free” nitrogen site and the proton concentration increases. The fall of the curve for the increasing  $x$  is associated with the relative excess of heterocycles which can hardly come across any free acidic group.

## 3. Benzimidazole intercalated polymer

In this section the available experimental data for the benzimidazole-based polymer proton conductors [10] are analyzed. For the pure polystyrene the glass-transition temperature is  $T_g = 95$  °C while for the polystyrene sulfonic acid (PSSA) is shifted to  $T_g = 140$  °C [19]. After intercalation of the PSSA within the BnIm, the  $T_g$  rises only slightly to 149 °C, hardly depending on the molar ratio  $x$ . When for the same polymer matrix the imidazole or triazole are dopants they act as plasticizers shifting the  $T_g$  values to lower temperatures [20]. Moreover, in such a case the  $T_g$  depends significantly on the molar ratio.

The BnIm is anchored to the polymer backbone by the covalent bond. The FT-IR spectra show that the  $\text{SO}_3\text{H}$  groups are deprotonated by doping with the benzimidazole and form  $\text{SO}_3^-$  groups [10]. This in turn shall increase the concentration of protons traveling along the conduction pathways with respect to the pure BnIm (one proton per one BnIm molecule). But since the highest current was measured at  $x = 1.5$ , it confirms the well-known fact that the intensive diffusion requires both a high charge density and a high defect density. Note that when the relative molar ratio grows, more and more heterocycles

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