



Relationship between hydrogen bond and viscosity for a series of pyridinium ionic liquids: Molecular dynamics and quantum chemistry

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ABSTRACT

The relationship between molecular structure and viscosity for four pyridinium ionic liquids is explored by combination of molecular dynamics and quantum chemistry. Our central aim is to study the relationship between hydrogen bond and viscosity. It is expected that a simple method would be built to judge the relative sequence of viscosity for a series of ionic liquids with similar structures. Although some items related with the viscosity are omitted, it is no doubt a direct method to estimate the range of viscosity. The methyl group substituted in *ortho* position would greatly increase the viscosity since more hydrogen bonds would be formed with stronger strength. While the pyridinium ionic liquids with the substitution in *meta* and *para* position has the similar viscosity, which is consistent with the similar features of hydrogen bonds in them.

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1. Introduction

The development of industry has greatly promoted the prosperity of human society in the past century. At the same time, the pollution problem becomes more and more serious with an unprecedented rate [1]. The focus on industry has been varied from product yield and quality to reduction of the industrial pollutants [2]. Organic solvent is one of the most important components in industrial pollutants [3]. However, it is also indispensable in various fields related with chemistry and chemical engineering [4]. Employment of the suitable alternative is the generic solution, which is better than pollute and remediate. Ionic liquids (ILs) are liquids at room temperature and regarded as possible replacement for organic solvents in various applications [5]. Moreover, ILs are expected to have no contribution to air pollution due to their negligible vapor pressures [6]. However, the viscosity of many ionic liquids is much higher than the common organic solvents [7], which greatly hinders their many practical applications including mass and heat transfer process and/or make it difficult for fluids pumping and stirring [8]. Nevertheless, viscosity of the ILs is an important factor to evaluate them [9].

One of the most promising advantages of ILs is their tailor-made characteristic [10]. By suitable combination of different ions, any ionic liquids with desired properties would be designed [11]. The accurate and reliable relationship between the molecular structure and their macroscopic properties is critical for the utilization of ILs at an industrial

level rather than at a laboratory scale [12]. Although available studies on different aspects of ILs have increased exponentially, most of them have focused on imidazolium ILs [13]. Relevant studies are still scarce for pyridinium ILs in view point of nanoscopic level. Normally, pyridinium ILs show larger viscosities than the equivalent imidazolium compounds [14] indicating that there are some deviations between them. It is no doubt that experiment is a direct and efficient method to obtain the accurate viscosity [15]. However, it is impossible to measure everyone since the number of synthesized ILs has been millions. Theoretical prediction is an alternative method to obtain the viscosity with a high promise between cost and result [16]. However, it is still time consuming to get the accurate value for viscosity of ILs by theoretical simulation method [17]. A popular method is to predict the relative sequence of viscosity for a series of ILs with similar structures. If the viscosity of one IL is known, the approximate region would be confirmed for others, which is enough to determine its suitable applications. Lots of theoretical studies have been devoted to building the structure-property relationship [18]. Aparicio and Atilhan have studied the viscosity for a series of pyridinium ILs by combination of experimental and theoretical methods [19]. It indicates that the viscosity of ILs is affected by complex factors including size, shape, and interaction energies for anion-cation pairs [20]. Some investigations have found that viscosity is greatly related with the hydrogen bond. If we would build a relationship between hydrogen bond and viscosity, there would be a possible simple method to predict the relative sequence of viscosity.

Here, the relationship between hydrogen bond and viscosity of four pyridinium ILs, 1-butyl-2-methylpyridinium tetrafluoroborate ([b2mpy][BF₄]), 1-butyl-3-methylpyridinium tetrafluoroborate ([b3mpy][BF₄]), 1-butyl-4-methylpyridinium tetrafluoroborate

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([b4mpy][BF₄]), *N*-butylpyridinium tetrafluoroborate ([bpy][BF₄]) (see Figs. 1–2) is studied to explore the effect of substituted group and position on the viscosity. The probability of hydrogen bonds is explored by the molecular dynamics (MD) simulation along with the quantum chemistry. Besides the single ionic liquid, the dimer of ionic liquids is considered to be taken as the example of the smallest cluster.

2. Computational details

2.1. Molecular dynamics

All MD simulations were carried out using the GROMACS 5.1.2 package [21]. The simulated systems were prepared in cubic boxes of approximate $10 \times 10 \times 10$ nm, containing 512 ion pairs for all of the studied ILs. The periodic boundary condition (PBC) was applied to all three dimensions of a cubic simulation box and a 1.5 nm cut-off was applied to the nonbonded interactions. The long-range electrostatic interactions were handled with the particle mesh Ewald (PME) method associated with long-range dispersion corrections [22]. Initially, the MD trajectories ran under the isothermal and isobaric ensemble at $T = 313.15$ K and $P = 0.1$ MPa, where the V-rescale thermostat (stochastic type) [23] and Parrinello-Rahman barostat were used with relaxation constants of 1.0 and 4.0 ps, respectively. The molecule was described by the General Amber Force Field (GAFF) [24]. The corresponding parameters are listed in Table S1. The bonds involving hydrogen atoms were constrained with SHAKE [25]. Due to the low-diffusion of ILs, the systems were heated up to 700 K for 1000 ps to keep the ion

mobility. And then the temperature was gradually decreased to 313.15 K for 1 ns. Finally, the production equilibrium was carried out for 30 ns, using a timestep of 2 fs and saving a configuration every 5000 timesteps.

2.2. Quantum chemistry

The electronic calculations were carried out by Gaussian 09 program [26]. Both single ion pair and two ion clusters were optimized by Becke's three parameter exact exchange-functional combined with Perdew and Wang (B3PW91) method [27,28] with 6-31G(d,p) basis set [29]. At the same level, the vibrational frequency was calculated to confirm that the optimized stationary point is the minimum with all real values.

3. Results and discussion

3.1. Site-site radial distribution functions (RDFs)

To testify the accuracy of employed force field, the densities of all ILs are calculated and listed in Table 1. All calculated densities are consistent with the experimental results [30–32] with the error less than 0.74%, which indicates that the employed force field is suitable for the studied ILs.

The hydrogen-bond interactions in all the investigated ILs are analyzed by site-site radial distribution functions (RDFs). To clearly present hydrogen bonds, their distances are tabulated in Table 2. Fig. 3 presents the RDF between various H atoms in cation and F1 atom in [BF₄] anion. It is worth to note that other three F atoms have the same chance to form

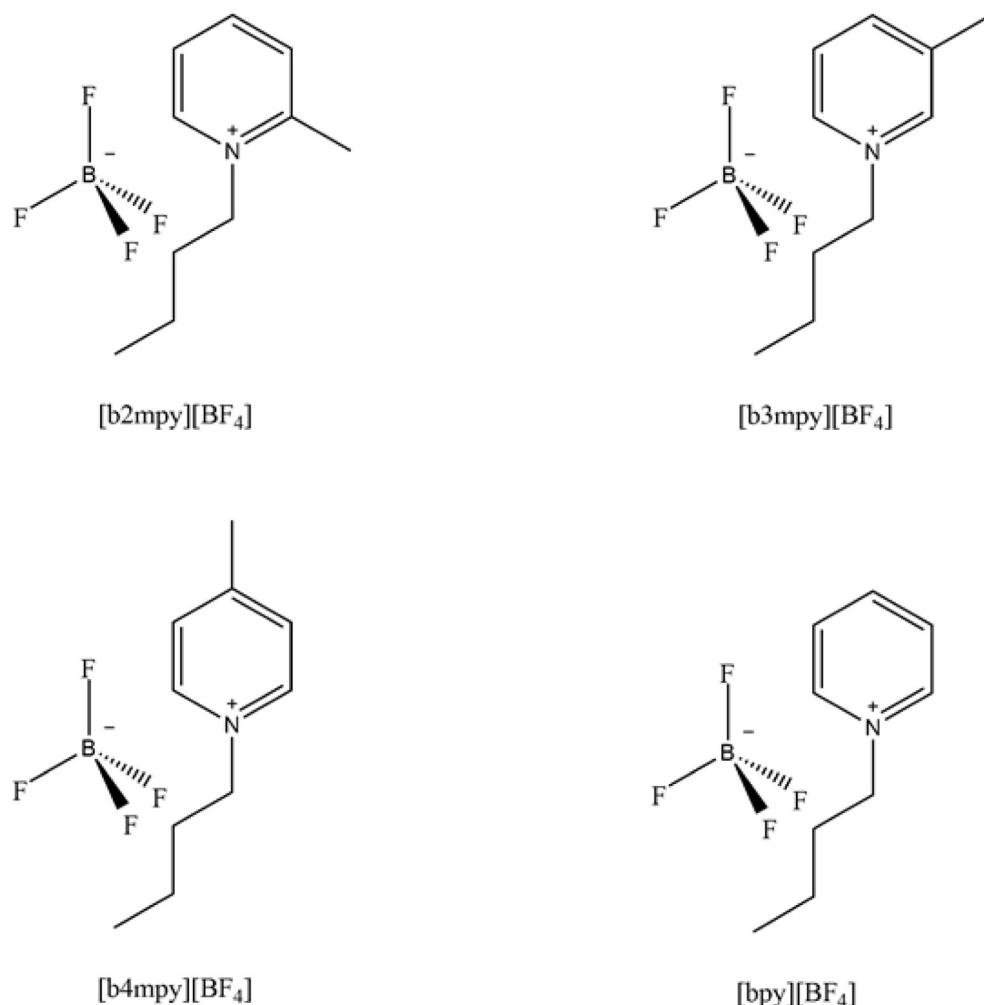


Fig. 1. Molecular structures of [b2mpy][BF₄], [b3mpy][BF₄], [b4mpy][BF₄], and [bpy][BF₄].

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