



Theoretical and experimental studies on proton transfer in acetate-based protic ionic liquids



Xuejun Sun^a, Bobo Cao^a, Xinming Zhou^b, Shuangyue Liu^a, Xiao Zhu^{a,*}, Hu Fu^{b,*}

^a School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China

^b College of Science, Chian University of Petroleum, Shandong, Qingdao 266580, China

ARTICLE INFO

Article history:

Received 5 March 2016

Received in revised form 13 May 2016

Accepted 25 May 2016

Available online 26 May 2016

Keywords:

Protic ionic liquids

Proton transfer

Interaction energy

FTIR spectra

NBO

AIM

ABSTRACT

In this study, the proton transfer of three protic ionic liquids (PILs) pyrrolidinium acetate ([Pyrrol]OAc), diethylammonium acetate ([DEA]OAc) and bis-(2-methoxyethyl)-ammonium acetate ([BMOEA]OAc) were investigated. At first, the structures of the ion-pairs and molecular pairs of these PILs were optimized at B3LYP/6-311++G(d,p) level. The interaction energy between anions and cations was also obtained. The proton transfer processes were verified by intrinsic reaction coordinate (IRC) pathways tracing to the energy profiles connecting the transition state (TS) to the two desired minima, i.e. ion pair and molecular pair. The experimental attenuated total reflection (ATR) FTIR spectra of these PILs at room temperature were determined and compared with the results calculated at B3LYP/6-311++G(d,p) level. Vibrational mode analyses (VMA) for [Pyrrol]OAc found that $\delta(\text{NH})$ has an imaginary frequency (-147.3 cm^{-1}), which is accounted for proton transfer from $[\text{NH}_2]^+$ to OAc^- . Natural bond orbital (NBO) analyses pointed out that second order perturbation stabilization energy of $(E(2))$ of $\text{LP}(\text{N}1) \rightarrow \sigma^*(\text{O}2-\text{H}5)$ was much larger than that of other orbitals, and should be the symmetrical matching with the maximum overlap and the minimum gap (0.73 au). The hybridized index of N atom is varied from $\text{sp}^{3.65}$ in ionic pair to $\text{sp}^{4.49}$ in TS. The constituent of s orbital decreases 3.3% and the length of N1-H5 increases from 1.02 Å in ionic pair to 1.65 Å in TS, and the symmetric stretching vibration takes place the red shift. It could be explained that the N1-O2-H5 played an important role in the stabilization of molecular pair. The electron density $\rho(r)$ and the Laplacian of the electron density $\nabla^2\rho(r)$ derived from atoms in molecules (AIM) analyses were used to describe the intensity and characteristic of a bond. The results indicate that a very strong interaction of the hydrogen bonds exists in the ion-pair geometries and the bonds are the covalent bond.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

As an important branch of ILs, protic ionic liquid (PIL) is mentioned frequently in recent years [1,2]. PILs is often prepared through the exchange of protons between a Brønsted acid and a Brønsted base [3]. Compared to aprotic ILs (AILs), PILs possess strong acidic protons [4–7] (acts not only as a donor, but also as an acceptor) as well as significant vapour pressure and so on, which can be easily prepared, purified and protonated [8]. The earliest report on PILs was in the end of 19th century [9,10]. Rebelo et al. [11] and Ballone et al. [12] had revealed that the vapour phase of AILs consists of ion pairs, with no detectable concentration of either free ions or larger clusters. Vaghjiani et al. [13] demonstrated the presence of intact ion pairs in the gas phase using mass spectrometry. Ohno et al. [14] revealed that protons in PILs transfer incompletely, the molecule pairs could coexist with ion pairs in the

gas phase. Recently, Li et al. [15] used EI-MS spectroscopy to analyse the compositions of gaseous ILs, and the study showed that the dynamic balance between ions and molecules could be controlled by the acidity. Since the EI-MS spectroscopy [14–17] experiments have confirmed the dynamic balance of the molecular pairs with the ionic pairs in the gas phase, the proton transfer from the ionic pairs to molecular pairs should happen. Through the investigation of the experimental results and theoretical calculations, we believe that a transition state (TS) exists in the proton transfer processes.

In this paper, the proton transfer processes in three acetate-based PILs, pyrrolidinium acetate ([Pyrrol]OAc), diethylammonium acetate ([DEA]OAc) and bis-(2-methoxyethyl)-ammonium acetate ([BMOEA]OAc) were investigated. The stable geometries and interaction modes of the cation, anion, ionic pair, TS and molecular pair have been obtained and characterized by density functional theory (DFT) calculations. The proton transfer from cation to anion can be observed and testified by the TS and intrinsic reaction coordinate (IRC) calculations. The lower energy barriers indicate that dynamic balance exists between the ionic pairs and molecular pairs. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra are used to detect the vibrational frequencies of the

* Corresponding authors.

E-mail addresses: sxsunxuejun@163.com (X. Sun), qfucabobo@163.com (B. Cao), zhouxinming@upc.edu.cn (X. Zhou), liushuangyue0919@163.com (S. Liu), qfmu_zx@163.com (X. Zhu), fuhui@upc.edu.cn (H. Fu).

ionic pairs and molecular pairs. The chemical nature of covalent bond and hydrogen bond as well as proton transfer process were analysed by the vibrational modes analyses (VMA), nature bond orbital (NBO) and theory of atoms in molecules (AIM). The results indicate that proton transfer process plays an important role in the physicochemical property of PILs.

2. Experimental methods

2.1. Synthesis of acetate-based PILs

Equivalent mol of Brønsted acid AcOH and Brønsted base [Pyrrol], [DEA] and [BMOEA] were added into a round-bottom flask simultaneously and stirred vigorously in acetone-dry ice bath to dissipate the exothermic heat, then the mixture was dried under vacuum for 24 h at 40 °C. The purities of the as-prepared PILs were determined by ¹H NMR and ¹³C NMR (Bruker AM 400 MHz spectrometer) spectra, and no impurities were found. The water contents of these PILs were determined by Karl-Fischer titration, which should be below 100 ppm.

2.2. ATR-FTIR spectra measurement

ATR-IR spectra were carried out at a Prestige-21 FT-IR spectrometer (Shimadzu, Japan) using a single reflection ATR cell. The results were obtained in the DTGS detector mode using an accumulation rate of 40 scans at a resolution of 4 cm⁻¹ in the spectral range of 400 to 4600 cm⁻¹ at room temperature. The FTIR spectrum measurement for each sample was repeated for three times.

3. Computation methods

All ground state and TS geometries were located by using hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-311++G(d,p) basis sets [18,19]. The chosen basis set contains diffuse functions that are required for the correct description of intramolecular hydrogen bonds [20]. No restrictions on symmetries were imposed on the initial structures, therefore the geometry optimization for the saddle points occurred with all degrees of freedom. All the geometries were optimized at B3LYP/6-31G(d,p) level and also characterized as minima by frequency analyses at first, then geometry optimizations were performed at B3LYP/6-311++G(d,p) basis sets level, followed by frequency calculations to verify the reasonability of the optimized structures. After that, the IRC pathways were traced to verify the energy profiles connecting the transition structure to the two desired minima of the proposed mechanism. Furthermore, the interaction energy (ΔE) including the basis set superposition errors (BSSE) [21] correction using the counterpoise (CP) [22] method was estimated. Finally, NBO and AIM analyses were performed using B3LYP/6-311++G(d,p) basis set to confirm the existence and characteristic of the hydrogen bond. All the DFT calculations were carried out with Gaussian 03 package [23].

4. Results and discussion

4.1. Geometries and electrostatic potential analyses

Geometries of [Pyrrol]⁺, [DEA]⁺, [BMOEA]⁺ and OAc⁻ were optimized at B3LYP/6-311++G(d,p) level in order to give a visual understanding on interactions before the design of initial geometries for the ion pairs. The structural parameters are shown in Table S1 (Electronic Supplementary information). The electrostatic potential (ESP) is a rigorously defined expectation quantity which is measured as the first-order interaction between the charge (electrons and nuclei) distribution and a positive unit charge at any point in space surrounding molecules and ions or solvents, and a real physical property that can be determined experimentally by diffraction methods, as well as computationally [24]. The ESP surface at sites close to the polar group is influenced by the

stereo structure and the charge density distribution. 3D plots of the ESP surface for above ions are given in Fig. 1. It indicates that the highly negative regions (red) of OAc⁻ anion are found around the polar oxygen atom of the carboxyl group and show high activity on the electronegative O atoms. In contrast, the highly positive regions (blue) in [Pyrrol]⁺, [DEA]⁺ and [BMOEA]⁺ are localized on the hydrogen atom of the amine groups, which can be considered as possible sites for nucleophilic attack of the oxygen atom.

The interaction energy (ΔE) is defined as the difference between the energy of the ionic system ($E_{ionpair}$) and the sum of the energies of the purely cationic (E_{cation}) and anionic (E_{anion}) species

$$\Delta E = E_{ionpair} - E_{cation} - E_{anion} \quad (1)$$

the interaction energies of [Pyrrol]OAc, [DEA]OAc and [BMOEA]OAc are 515.05, 505.38 and 499.76 kJ/mol, respectively. It can be found that all of the interaction energies between cation and acetate anion are around 500 kJ/mol. They are much larger than the normal hydrogen bond energy (50 kJ/mol), which indicate the existence of strong electrostatic attractions between cations and acetate anion [25]. The maximum value of the interaction energies is ion pair of [Pyrrol]OAc, the reason is that the hydrogen atom in N1 atom possessing larger positive charge. For [BMOEA]OAc ion pair, the interaction energies decreases along with the increasing alkyl chain length.

4.2. Proton transfer process

The equilibrium of proton transfer process exists in acetate-based PILs, which can be expressed as



where HB⁺ and A⁻ are Brønsted acid of B and Brønsted base of HA, respectively. For acetate-based PILs, the equilibrium constant is not very large. The PIL contains not only ionic pair but also molecular pair to form a complex system. The interaction energies of HB⁺ and A⁻ are very large, corresponding to Coulomb force. HA and B are neutral species, the interaction energies among them are smaller, corresponding to hydrogen bonding and *van der Waals* forces. This is why PILs have a vapour pressure [3,16].

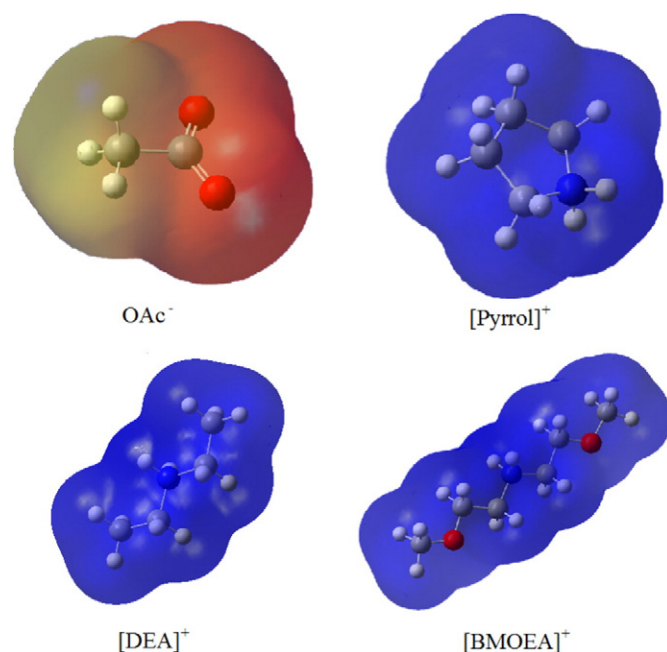


Fig. 1. The 3D plots of the electrostatic potential surface for four kinds ions, respectively.

Download English Version:

<https://daneshyari.com/en/article/5409783>

Download Persian Version:

<https://daneshyari.com/article/5409783>

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