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Hydrogen bonding interactions in nicotinamide Ionic Liquids: A comparative spectroscopic and DFT studies

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ABSTRACT

Being biodegradable in nature nicotinamide based Ionic Liquids (ILs) are gaining much attention now a day. Nicotinamide iodide (i.e 1-methyl-3ethoxy carbonyl pyridinium iodide (mNicI)) and 1-methyl-3ethoxy carbonyl pyridinium trifilimide ($mNicNTf_2$) new ILs has been synthesized and has been characterized using different spectroscopic techniques like NMR, UV visible and infrared spectroscopy. Theoretical studies have been performed on several nicotinamide ILs. Geometry and spectral features were further characterized by Density Functional Theory (DFT) calculation. NBO charge distribution and electrostatic potential diagram presents in depth knowledge about interactions between cation and anion. A comparative theoretical study between mNicI and its other analogues i. e 1-methyl-3 ethoxy carbonyl pyridinium chloride and bromide i. e mNicCl and mNicBr has also been performed. C—H···X hydrogen bonding along with C···X interaction has been reported for the first time for the nicotinamide based ILs. C2—H stretching frequency shifts to higher wavenumber with change to a lesser electronegative anion. mNicCl and mNicBr are expected to be solid in nature with the evidence from the red shift in stretching frequency as compared to mNicI. TD-DFT calculation of mNicI proved that pale yellow color of liquid is due to inherent transition from anion to cation.

1. Introduction

Research in the area of Ionic Liquids (ILs) continues to grow and their applications have broadened extensively now a days. ILs is of enormous importance as a huge amount of different ILs can be envisioned by the simple combination of different anions and cations. By varying the anion species or the cation entity (e.g. varying alkyl chain or the core), it is possible to change the physical properties as hydrophobicity, viscosity, density, and solubility and thus its influence towards the biological features [1]. Non-volatile nature of ILs under equipped conditions minimizes their effect on air quality during their life cycle in a chemical reaction. However, impact of ILs on soil and water is definitely of considerable concern at the time of their disposal. Hence using the technique to tune the properties of ILs as function of the chemical structure, one can design the ILs that would not just be ideal solvents for chemical processes, but would also be safe for disposal and would therefore be sustainable [2]. In this respect after a thorough study of Pyridinium based ILs by Harjani et al. the biodegradation of pyridine based ILs showed noticeably high levels of biodegradability over the 28 days period. Thus this study illustrate that the structural variation in the pyridinium skeleton may lead to the formation of desirable ILs which possess good solvent attributes and a tendency to biodegrade when released into an aquatic environment [3]. In this paper, we focused our attention on the ILs that were based on the ester moiety, as the introduction of this group in the pyridinium based ILs improved their biodegradation probably by providing a site for an enzymatic attack [4]. Hence our objective is to do synthesis and characterization of new pyridinium based IL which is supposed to be an efficient biodegradable solvent [5]. Synthesis and characterization of 1-methyl-3-ethoxy carbonyl pyridinium iodide (commonly called nicotinamide iodide, mNicI) and 1-methyl-3-ethoxy carbonyl pyridinium trifilimide ($mNicNTf_2$) ILs has been carried out and in-depth structural studies has been performed using DFT along with IR and NMR spectroscopic studies. C—H···X hydrogen bonding along with C···X interaction has been reported for the first time for the nicotinamide based ILs. Natural bond orbital (NBO) analysis was also performed to find out the charge transfer and the interaction between cation and anion. Pale yellow color of mnicI has been explained by using TDDFT calculation. Experimental observations have been well reproduced with the theoretical findings.

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2. Methodology

2.1. Reagents and instrumentation

Acetonitrile (HPLC grade) was procured from Merck, Germany and were used after purification following standard procedures. UV–Visible spectra were measured by CARY 100 BIO UV– Visible Spectrophotometer, which has photometric linearity till absorbance 3.5. Infrared spectrum of products was measured with Varian FTIR 3100 in the region 400 cm^{-1}–3500 cm^{-1} using neat sample. 300 MHz NMR (JEOL) was used to measure the ^1H NMR.

2.2. Synthesis of 1-methyl-3-ethoxy carbonyl pyridinium iodide (mNicI)

Scheme for the synthesis of mNicI is shown in Fig. 1. 25.0 mL toluene was taken in a round bottom (RB) flask, and 4.5 mL of ethyl nicotinate was added under inert atmosphere. To it 2.5 mL methyl iodide was added in inert atmosphere and was stirred at room temperature for 6 h in the beginning but no progress was monitored. Hence temperature was increased to 45 °C and stirred for 24 h. Viscous yellow liquid was separated from solvent. Solvent was decanted and yellow viscous liquid was washed with diethyl ether (2 × 20.0 mL). After that 25.0 mL acetonitrile was added and RB flask was shaken till viscous liquid dissolved completely. It was taken in 250.0 mL separating funnel and diethyl ether (70.0 mL) was added. The yellow viscous liquid started settling down. It was shaken thoroughly and allowed to stand for 15 min. The yellow viscous liquid was collected in a 50.0 mL peer shaped vessel and was added with 70.0 mL diethyl ether. Again it was washed with diethyl ether and decanted. A highly viscous liquid was obtained. The yellow color ionic liquid thus obtained was kept under reduced pressure for 24 h. Precautions were taken to eliminate the presence of water or organic solvents in the purified IL. At 45 °C temperature, there is uncertainty of presence of impurities which is responsible for the color of the ILs, but the yellow color of mNicI was explained in our later section by TD-DFT calculation. The product was confirmed by IR (Supplementary Fig. S1) peak positions observed at 668 cm^{-1}, 749 cm^{-1}, 1188 cm^{-1}, 1307 cm^{-1}, 1730 cm^{-1}, 3042 cm^{-1} and ^1H NMR (Figure S2a,b and c) (in $CDCl_3$ ppm); 1.45–1.49 (q,3H), 4.48–4.55 (q,2H), 4.80 (s,3H), 8.29–8.34 (t,1H), 8.91–8.89 (d,1H), 9.36 (s,1H), 9.76–9.78 (d, 1H). As we know that halide based ILs are very much sensitive to water (moisture present in atmosphere) [6,7] a broad peak at 3445 cm^{-1} refers to water present in mNicI ILs. Although the reaction has been carried out in inert atmosphere (to avoid the moisture effect) and water is not used anywhere in the reaction, effect of water expected to be lesser.

2.3. Synthesis of 1-methyl-3-ethoxy carbonyl pyridinium trifilimide (mNicNTf$_2$)

Scheme for the synthesis of mNicNTf$_2$ is shown in Fig. 2. In 15 mL of water, 2 g (6.8 mmol) of mNicI was added. The solution

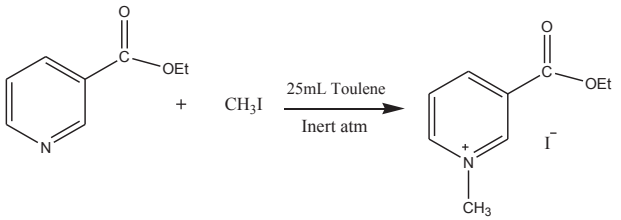

Fig. 1. Scheme for synthesis of 1-methyl-3-ethoxy carbonyl pyridinium iodide (mNicI).

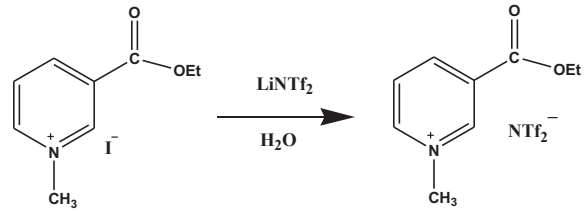

Fig. 2. Scheme for synthesis of 1-methyl-3-ethoxy carbonyl pyridinium iodide (mNicNTf$_2$).

was treated with 2.2 g (7.5 mmol) of aqueous lithium triflimide and the resulting mixture was stirred at room temperature for 3 h. The water immiscible triflimide based ionic liquid separated from aqueous solution was extracted with dichloromethane (3 × 20 mL). The combined extracts were dried over anhydrous sodium sulfate and evaporated under reduced pressure to yield the corresponding triflimide anion based ionic liquid. The light yellow colored liquid thus obtained was further dissolved in 10 mL of pure and dried acetonitrile (ACN) to treat with activated charcoal for decolorization. The mixture was stirred for 4 h followed by filtration through a sintered column packed with fresh charcoal and alumina. The resultant solution was evaporated on rotavapour at 50 °C and at reduced pressure to get colorless liquid product. IL thus obtained was kept under reduced pressure (10^{-3} bar) for 24 h at room temperature. Yield is 86.6%. Characterization of above product done using IR (Figure S3) and ^1H NMR (Figure S4a,b and c) spectroscopy. Peak at 1057 cm^{-1}, 1137 cm^{-1}, 1190 cm^{-1}, 1351 cm^{-1}, 1737 cm^{-1}, 3093 cm^{-1} and 3401 cm^{-1} confirms the required product. A very weak peak at 3401 cm^{-1} refers to very little amount of water present in mNicNTf$_2$ IL. ^1H NMR (Figure S4a,b and c) (in $CDCl_3$ ppm); 1.38–1.47 (q,3H), 4.45–4.53 (q,2H), 4.55 (s,3H), 8.12–8.17 (t,1H), 8.86 (d,1H) 8.95–8.97 (d,1H), 9.17 (s, 1H) confirms the required synthesized product.

2.4. Computational detail

All the calculations were performed using **Gaussian 09** program [8]. The hybrid Becke3-Lee-Yang-Parr (B3LYP) exchange correlation functional [9,10] with 6–31++ G (d,p) basis set was employed for C, H, N, O, Cl and Br atoms but for I, larger basis set DGDZVP was employed [11]. No restriction on symmetries were imposed on the structure, therefore geometry optimization for saddle point occurred with all degrees of freedom. The optimized structures were then subjected to frequency calculation to verify the reasonability of optimized structures and so as to get the vibrational frequency. Interaction energy is the difference between the energy of the ion pairs system (E_{AX}) and the sum of the energies of the purely cationic (E_{A+}) and anionic (E_{X-}) species (vide equation (1)) [12].

$$\Delta E(KJ/mol) = 2625.5[E_{AX}(\alpha u) - (E_{A^+}(\alpha u) + E_{X^-}(\alpha u))] \quad (1)$$

Finally TD-DFT calculation done to get obtain the energy, oscillator strength and wavelength and was correlated with the experimental UV–visible spectrum.

3. Results and discussion

3.1. Geometry optimization and H-bonding interaction

The schematic diagram of 1-methyl-3-ethoxy carbonyl pyridinium halide (mNicX) is shown in Fig. S5. 1-methyl-3-ethoxy carbonyl pyridinium iodide and its analogues chloride and bromide (mNicX, where X = Cl^-, Br^-, I^-) was optimized at B3LYP level. The