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Influence of various anions and cations on electrochemical and physicochemical properties of the nanostructured Tunable Aryl Alkyl Ionic Liquids (TAAILs): A DFT M06-2X study

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ABSTRACT

The capability to adjust the properties of ILs by combining different cations and anions leads to the name of “designer solvents” for ILs. There is a steadily growing interest for the use of ILs in electrochemical applications such as supercapacitors and rechargeable batteries. In this work, the highly parameterized, empirical exchange–correlation functional at M06–2X/6-311++G(d,p) level of theory were employed to investigate the influence of various cations and anions on electrochemical and physicochemical properties of the thirty-six ILs formed from a combination of para–X–phenyl methylimidazolium ($[X{-}PhMIM]^+$: $X = NH_2$, OH, OCH_3, CH_3, H, F, CHO, CN and NO_2) cations and the four different conventional anions ($Y_{1-4} = CH_3COO^-$, NO_3^-, BF_4^- and PF_6^-). The potentials of the cathodic (V_{CL}) and anodic (V_{AL}) limits, electrochemical windows (ECW), CT values, volumetric and thermodynamic properties, interaction energy, enthalpy of formation of cations, Gibbs free solvation energy, topological properties and NMR one- and two bonds spin–spin coupling constants (SSCCs) were predicted.

1. Introduction

Ionic liquids (ILs) are one of the most promising classes of new materials investigated in the last decade. They are typically composed of large asymmetric organic cations and various inorganic or organic anions that exist in the liquid state at room temperature [1,2]. ILs exhibit interesting and sometimes unusual physical properties such as vanishing vapor pressure, low melting point, non–flammability, favorable solvation behavior, controllable hydrophobicity, resistant to oxidation and extraordinary high thermal/chemical/electrochemical stability in the presence of air and moisture, in contrast to the characteristics of traditional volatile organic solvents [3–15]. Ionic liquids also show substantial potential for use in advanced electrochemical devices [16–19], energy technology [20,21], optics [22,23], environmental chemistry [24,25], medicine [26] and nanotechnology [27–29]. Especially, there is a steadily growing interest in use of room-temperature ionic liquids (ILs) as electrolytes in electrochemical applications such as supercapacitors [30–32] and rechargeable lithium batteries [33–37].

Room-temperature ILs have acquired increasing interest as electrolytes in electrochemical applications. In the search of higher energy density storage systems, the electrochemical windows (ECW) of current electrolytes are a limiting factor. A wide ECW makes ILs promising electrolytes for electrochemical applications. Many ILs have wide electrochemical windows of approximately 5–6 V [16,38] and even an enlarged ECW, up to 7 V, was found for $[BMIm][BF_4]$ and $[BMIm][PF_6]$ by Goncalves et al [39], which are considerably larger than that of current organic electrolytes. The electrochemical window is determined experimentally by performing a linear sweep voltammetry using inert electrodes (e.g. Pt or Au) and measuring the cathodic or anodic currents, which are indicative of electrolyte reduction or oxidation. However, measured electrochemical windows depend heavily on the measurement conditions (e.g. type of electrode) [37,40]. Computational chemistry techniques can contribute to a more focussed development of ILs for electrochemical applications [41]. Recently, Tunable Aryl Alkyl Ionic Liquids (TAAILs) based on 1-aryl-3-methylimidazolium salts have been introduced by Ahrens et al. [42,43]. As a new generation of ionic liquids, the physicochemical properties of TAAILs determine their performance in practical applications. Similar to standard ILs, the properties of TAAILs can also be tuned by proper selection of a suitable cation/anion pair. Also, different substituents (electron-donor and electron-acceptor groups) and substituents position (ortho, meta and para positions)

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[44,45] at aryl ring of TAAILs can significantly influence the properties and performance of ILs such as melting point, thermal stability, sensitivity and etc. TAAILs have asymmetric cation and contain mesomeric and inductive effects by having C_{sp2} and C_{sp3} at their cations structures, allows a far greater variation of the ionic liquids characteristics than imagined compared with the usual ILs.

Many methods have been developed to explore the anion–cation interactions of ILs, including experimental [46–54] and theoretical [55–66] methods. It is, however, time-consuming and cost- intensive to study the physical properties of all ILs by experiments. Thus, theoretical study of special and tunable properties of ILs is an efficient and necessary approach.

One of the most attractive characters of TAAILs is that their properties can change with the combination of different anions and various substituents (electron-donor and electron-acceptor groups) on the phenyl ring of the cations, which provides the chances for designing and developing TAAILs with excellent properties. Accordingly, we have chosen anions of stronger basicity such as CH_3COO^- and NO_3^- and lower basicity such as PF_6^- and BF_4^- for investigation of the nanostructures of phenyl methyl imidazolium–based ionic liquids. One possible strategy for future IL Li-battery electrolyte development would be to functionalize existing cations with electron-donor groups to achieve better cathodic stability [37]. To the best our knowledge, interaction between [para−X−phenyl methyl imidazolium]$^+$ cations and above anions has not been characterized and no detailed studies exist on the influence of different anions and various substituents in the para position of these cations on hydrogen bonding strength between their constituents. The substituents selected for this study cover almost the whole set of classical substituents: from the strongly electron-attracting (NO_2, CN, CHO and F) to typical electron-donating (NH_2, OH, OCH_3 and CH_3) ones. In the present work, binding energy between these cations and anions, geometrical parameters and topological properties, Gibbs free energy of formation in the gaseous phase and the different mediums and electrochemical stability of mentioned ILs based on their electrochemical window values were explored. In addition, we characterize nature of intermolecular interactions in TAAILs by natural bond orbital (NBO) [67] and Bader's quantum theory of atoms in molecules (QTAIM) [68] to provide a deeper understanding of the effect of the electron-attracting and electron-donating groups and nature of anions on the interaction between cations and anions, and the subsequent impact on their physicochemical properties. In addition, our approach also provides information on the species (cation or anion) contributing to the redox stability of the overall liquid. The results obtained in our work could provide insights on which substituents can be attached to cation such that the electrochemical stability is improved.

2. Computational details

In the past decade, density functional theory (DFT) is widely used to study the energy, structure, electronic properties and characterization of the nature of intermolecular interactions in ionic liquids [69–75]. Performance of a range of DFT functionals has been recently described to identify the most adequate in providing ionic liquids binding energies [76–84]. In this work, all of the structures of ion pairs were fully optimized using M06−2X [85–87] methods in conjunction with the 6−311++G(d,p) basis set [88,89]. To characterize the stationary points and calculation of zero-point vibrational energy (ZPVE) as well as thermochemical quantities, vibrational frequency analysis were performed at mentioned level of theory. The counterpoise method (CP) [90] was used to correct for basis set superposition error (BSSE) in the calculation of interaction energies. All the above calculations were performed by using GAMESS [91] and Gaussian 03 [92] programs.

The NBO analysis [93] was carried out on the M06−2X/6-311++G(d,p) wave functions using version 3.1 of NBO package [94]. Topological properties of electron charge density [electron density, $\rho(r)$, Laplacian of electron density, $\nabla^2\rho$ (r), and electronic energy density, H(r)] were also performed by the AIM2000 program package [95] at M06−2X/6-311++G(d,p) level of theory. Density of states (DOS) in [X–PhMIM][Y_{1-4}], (X = NH_2, OCH_3, H, CHO and NO_2) ion pairs was calculated using M06-2X functional.

In addition, the solvent effect on the stability of ion pairs (IPs) was examined by applying the polarizable continuum model PCM [96–98] at M06−2X/6-311++G(d,p) level of theory using optimized structures obtained in the gas phase. The PCM method defines the cavity from a set of overlapping spherical atoms having the appropriate van der Waals radii. The standard Gibbs free energy change ΔG°_{solv} for solvation of the solute species M in solvent S can be separated into $\Delta G^\circ_{solv} = \Delta G^\circ_{el} + \Delta G^\circ_{noel}$. The electrostatic contribution ΔG°_{el} to ΔG°_{solv} results from the electrostatic interactions between the solute and solvent and can be found from an SCRF calculation [99]. The non-electrostatic contribution (ΔG_{noel}) can be split into $\Delta G_{noel} = \Delta G_{cav} + \Delta G_{dis} + \Delta G_{rep} + \Delta G_{mm}$ where they are cavitation, dispersion, repulsion and molecular motion contributions to non-electrostatic energy, respectively. The molar volume of the TAAILs was calculated at 298 K using COSMO-RS method at BVP86/TZVP level. The $\Delta H^\circ_{f,g,298}$ and $\Delta G^\circ_{f,g,298}$ values of cations were calculated using the CBS-QB3 method.

Spin–spin coupling constants involving ^{13}C, ^{15}N, ^{17}O, ^{19}F, ^{31}P, ^{11}B and ^{1}H in all ion pairs and subunits were computed at M06−2X/6−311++G(d,p) level of theory. In the calculations presented here, all four terms FC, SD, PSO, and DSO that contribute to nuclear SSCCs in non-relativistic theory have been calculated.

3. Results and discussion

In this work, we will investigate the influence of different anions and substituents (electron-donor and electron-acceptor groups) in the para position of X-phenyl methyl imidazolium cations on the structural and electronic properties of TAAILs [X_{1-9}−PhMIM][Y_{1-4}] (X_{1-9} = NH_2, OH, OCH_3, CH_3, H, F, CHO, CN, NO_2 and Y_{1-4} = CH_3COO^-, NO_3^-, BF_4^-, PF_6^-). There are a significant number of possible interaction sites around the substituted cations that anions can be approached. The most stable nanostructures obtained for ion pairs are represented in Fig. 1. This figure shows that [Y_3] and [Y_4] locate above the imidazolium ring (on-top configuration), while [Y_1] and [Y_2] locate nearly in the plane of the imidazolium ring and are generally more close to the C2–H (in-plane configuration). It should be noted that the [X-PhMIM][Y_2] ion pair adopts the both configurations so that **A** structure is more stable than **B**.

3.1. Interaction energy

The physicochemical properties of the solutions are always determined by the intermolecular interactions. Although ILs are composed of ions completely, ion pairs as the fundamental structural units are very important in exploring ILs. The structures of anions and possible configurations (on-top and in-plane of anions) have many effects to the interaction energy of ILs.

The interaction energies ($U_{int} = \Delta E_0^{BSSE}$), Gibbs free interaction energy ($\Delta G_g = \Delta G_0^{BSSE}$) and interaction enthalpy ($\Delta H_g = \Delta H_0^{BSSE}$) of the [X−PhMIM][$Y_{1-4}$], (X = NH_2, OH, OCH_3, CH_3, H, F, CHO, CN, NO_2) ion liquids in the gas phase are reported in Table 1. As can be observed, the BSSE- and ZPVE-corrected interaction energies rang from (−112.1, −99.9, −99.8 and −94.8 kcal/mol) to (−102.1, −91.1, −90.0 and −85.9 kcal/mol) in [X−PhMIM][Y_{1-4}]