



Halogenation of imidazolium-based ionic liquids: Thermodynamic perspective



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ABSTRACT

Imidazolium cations are promising for anion exchange membranes, electrochemical applications and gas capture. They can be chemically modified in many ways including halogenation. Halogenation possibilities of the imidazole ring constitute a particular interest. This work investigates fluorination and chlorination reactions of all symmetrically non-equivalent sites of the 1-ethyl-3-methylimidazolium cation. Halogenation of all carbon atoms is thermodynamically permitted. Out of these, the most favorable site is the first methylene group of the side alkyl chain. In turn, the least favorable site is carbon of the imidazole ring. Temperature dependence of enthalpy, entropy, and Gibbs free energy at 1 bar is discussed. The reported results provide an important guidance in functionalization of ionic liquids to foster search of task-specific compounds.

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1. Introduction

Imidazolium-based ionic liquids (ILs) remain at the spotlight of chemists and physicists during the last years [1–3]. These ILs are actively investigated for applications in electrochemical devices, gas capture and anionic membranes [4–9]. The imidazolium cations can be coupled with many organic and inorganic anions to provide reasonable tuning of their physical chemical properties [10–17]. Apart from that, the imidazolium cation can be modified chemically. For instance, versatile functional groups can be grafted to the alkyl chains. Length and flexibility of these chains can be tuned. The ethyl, butyl, hexyl, octyl, decyl chains are widely explored around the world [14,17,18]. Addition of a single methylene group results in a significant shear viscosity increase and melting or glass transition temperature adjustment. Asymmetric chains of the IL cations play an important role in prohibiting their crystallization, because an energetically favorable crystalline structure becomes impossible.

Halogenation is a well-recognized pathway to modify properties of organic compounds. Many representatives of the family of chlorinated hydrocarbons are omnipresent in chemical laboratories as organic solvents. Fluorination and subsequent polymerization of ethylene resulted in polytetrafluoroethylene, the best known commercial brand of which is Teflon. Carbon fluoride is an extremely stable gas with a low boiling point. It is sometimes

used as a low temperature refrigerant. Due to its physical properties, carbon tetrafluoride does not deplete ozone layer and contributes to the greenhouse effect. Halogenation changes interaction sites of the compound. For instance, fluorination or chlorination of the imidazole ring will prohibit hydrogen bonding with the applicable anions and molecular co-solvents. This would have drastic consequences on the derivative ILs, such as different shear viscosity and different phase behavior. Even if a protic solvent is used, hydrogen bonding is not possible due to an insufficient electron density on the halogen atom because the imidazole ring of the cation is electron deficient. Fluorination of the hydrocarbon chains is also interesting, since it allows to obtain even more asymmetric cations exhibiting less favorable crystalline arrangements.

Thermodynamics of ionic liquids is currently widely studied using a large collection of theoretical and experimental techniques [19–31]. Almantariotis and coworkers [27] reported solubility and thermodynamics of solvation of carbon dioxide uptake by the imidazolium-based ionic liquids, 1-octyl-3-methylimidazolium bis[trifluorosulfonyl]imide (TFSI), 1-decyl-3-methylimidazolium TFSI and 1-(3,3,4,4,5,5,6,6,7,7,8,8,8)-tridecafluorooctyl)-3-methylimidazolium TFSI. The properties were determined experimentally at atmospheric pressure and between $T = (298 \text{ and } 343) \text{ K}$. According to the authors, carbon dioxide solubility is systematically higher in the fluorinated ionic liquid. Carbon dioxide solubility is also higher in the imidazolium IL with a longer hydrocarbon chain. Note, however, that no fluorination of the imidazole ring was performed in this work. It is interesting which consequences such a functionalization trick would have.

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Carvalho and coworkers [25] support the claim that adsorption of sour gases can be adjusted by fluorination of ILs. These authors considered (gas + liquid) equilibrium of 1-butyl-3-methylimidazolium acetate 1-butyl-3-methylimidazolium trifluoroacetate with carbon dioxide at temperatures up to 363 K and external pressures up to 76 MPa. Both anions exhibit a simultaneous interaction of the two oxygen atoms of the carboxylate group with CO₂. However, acetate acts as a stronger Lewis base than trifluoroacetate. This was confirmed by ab initio calculations using a reliable electron-correlation post-Hartree-Fock method.

Li and coworkers [21] synthesized novel hydrophobic ILs having performed partial substitution of chlorine and fluorine in the 1-butyl-3-methylimidazolium cation, C₈N₂H₁₅, via direct chlorine gas treatment and potassium fluoride, respectively. The following two compounds were characterized, [C₈H_(12.28)Cl_(0.96)F_(1.76)N₂] chloride and [C₈H_(12.75)Cl_(1.58)F_(0.67)N₂] hexafluorophosphate. According to these authors, chlorination mainly takes place in the imidazole ring and in the methyl group of the butyl chain. Shear viscosity and hydrophobicity of both halogenated derivatives increased greatly, while the decomposition temperature decreased to certain extent.

Shiflett and Yokozeki made an essential contribution in the development of task-specific imidazolium-based ILs and investigated their properties and phase behavior issues upon gas capture [32,33]. Brennecke and Maginn put significant efforts into a systematic molecular design of high-capacity, low-viscosity ILs to enhance carbon dioxide capture [34,35].

This work investigates halogenation (fluorination and chlorination) of the imidazolium-based ILs from the thermodynamics perspective. We identify five chemically non-equivalent prospective halogenation sites in the 1-ethyl-3-methylimidazolium cation. Not only halogenation of side hydrocarbon chains was considered, but also halogenation of the imidazole ring was probed. The substitutional halogenation was shown to be thermodynamically permitted in all cases, whereas fluorination appeared much more energetically favorable than chlorination.

Highly accurate gas-phase ab initio coupled-cluster electronic structure calculations were used to obtain molecular partition functions, which can be further processed to obtain thermodynamic quantities, such as enthalpy, entropy, free energy of reaction and their temperature dependences. Demand for thermodynamics data far exceeds current capabilities of the available experimental measurements. Numerical techniques to estimate gas-phase thermodynamics are able to provide certain assistance, that appears of great help for scheduling proper chemical syntheses and interpretation of the already generated experimental data.

2. Methodology

This work reports enthalpy *H*, entropy *S*, and Gibbs free energy *G* for the halogenation reactions involving the imidazolium-based cation. Temperature dependences of each thermodynamics potential are discussed over the range between *T* = (200 and 500) K. They may constitute interest for practical applications. Note that the imidazolium cations are thermally rather stable, whereas thermal decomposition of the imidazolium-based ILs normally starts from the anion.

Ab initio calculations do not directly produce enthalpies of formation or any other thermodynamic functions. Instead, they produce total molecular energies, electron energy levels, and optimized electronic structures. The total potential energy is negative and represents changes upon assembling a particle from multiple nuclei and electrons. Entropies, heat capacities, and other quantities are derived from the computed molecular partition function using equations of statistical mechanics. Enthalpy of for-

mation can be derived by computing the energy change for the selected chemical reaction. All thermodynamic predictions computed in this way correspond to an ideal gas. The major errors are expected to come from an electronic energy contribution, therefore electron correlation must be described thoroughly to obtain trustworthy results.

An electronic structure of all systems was optimized using the coupled-cluster technique. The coupled-cluster technique [36] is a numerical algorithm, which is used to describe many-body electronic systems and belongs to the group of post-Hartree-Fock methods. The molecular orbitals obtained from conventional one-electron Hartree-Fock calculations are used to construct multi-electron wave functions by means of an exponential cluster operator. This allows to explicitly account for electron-electron correlations, which are critically important for thermodynamic potentials derived from an electronic partition function. This method provides highly accurate energies and, consequently, molecular geometries. However, the underlying computational cost is much higher than that of Hartree-Fock and density functional theory computations. The coupled-cluster method cannot be used for sufficiently large systems, such as inorganic crystals with periodic structures. The implementation of coupled-cluster employed in the present work uses single and double substitutions from the Hartree-Fock determinant. Furthermore, it includes triple excitations non-iteratively to get a total potential energy [37].

The 6-311++G** Pople-type basis set was applied. This is a comprehensive split-valence triple-zeta polarized basis set, where polarization and diffuse functions are supplemented to all atoms. No pseudopotentials were applied. That is, all electrons were considered explicitly at all calculation steps. The wave function convergence criterion at every self-consistent field (SCF) step was set to 10⁻⁸ Hartree. No additional techniques to enhance the convergence were applied. The implementation of the outlined electronic structure methods in GAMESS [38] was employed.

3. Results and discussion

Figure 1 depicts prospective positions of the halogen substitution. Positions “CH₃”, “Et”, and “CH₂” correspond to alkyl chains, which are grafted to both nitrogen atoms of the imidazole ring. Positions “CR” and “CW” correspond to the carbon atoms within the imidazole ring. All these substitution reactions must be doable according to conventional chemical wisdom. However, it is unclear without a comprehensive numerical analysis, which reaction site is more preferable and which is less preferable. Especially, the differ-

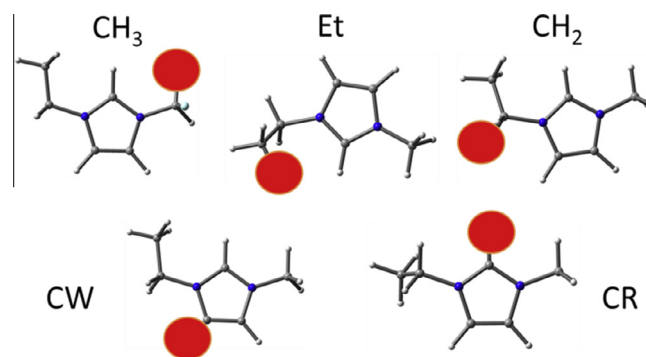


FIGURE 1. Halogen substitution sites in the 1-ethyl-3-methylimidazolium cation. Carbon atoms are gray, hydrogen atoms are white, nitrogen atoms are blue, and the halogen (fluorine, chlorine) atom is red. Five symmetrically non-equivalent carbon atoms were studied. As it will be shown below, these sites are also thermodynamically non-equivalent. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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