

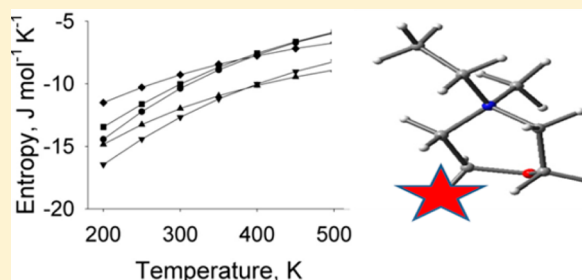
Are Fluorination and Chlorination of Morpholinium-Based Ionic Liquids Favorable?

Vitaly V. Chaban^{*,†} and Oleg V. Prezhdo[‡]

[†]Instituto de Ciência e Tecnologia, Universidade Federal de São Paulo, 12231-280 São José dos Campos, SP Brazil

[‡]Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

ABSTRACT: Room-temperature ionic liquids (RTILs) constitute a fine-tunable class of compounds. Morpholinium-based cations are new to the field. They are promising candidates for electrochemistry, micellization, and catalytic applications. We investigate halogenation (fluorination and chlorination) of the *N*-ethyl-*N*-methylmorpholinium cation from the thermodynamics perspective. We find that substitutional fluorination is much more energetically favorable than substitutional chlorination, although the latter is also a permitted process. Although all halogenations at different locations are possible, they are not equally favorable. Furthermore, the trends are not identical in the case of fluorination and chlorination. We link the thermodynamic observables to electron density distribution within the investigated cation. The reported insights are based on the coupled-cluster technique, which is a highly accurate and reliable electron-correlation method. Novel derivatives of the morpholinium-based RTILs are discussed, motivating further efforts in synthetic chemistry.



INTRODUCTION

Room-temperature ionic liquids (RTILs) are actively investigated in various branches of pure and applied science.^{1–4} They are employed as universal solvents, electrolytes, catalysts, and reaction media. RTILs are used in separation applications, fuel and solar cells, gas capture, and even biotechnology.^{1–19} Because of their specific structural properties, RTILs cannot form an energetically favorable crystalline lattice. Consequently, they exist in the liquid state over an unusually wide temperature range. A single cation can be coupled with numerous anions, providing a universe of novel compounds with tunable physical-chemical properties.

Most RTILs are based on heterocyclic organic molecules, such as imidazole, pyrrolidine, pyridine, piperidine, etc. Both protic and aprotic RTILs can be synthesized in many cases. Protons belonging to cations play an important role in formation of cation–anionic and cation–molecular hydrogen bonds. Hydrogen bonds are able to adjust physical properties of the solvent drastically. Morpholinium-based RTILs^{20–23} have been characterized recently. They have obtained significant attention because of their specific structural properties.²³ Morpholinium-based cations are bipolar owing to simultaneous presence of oxygen (electron-rich center) and nitrogen (electron-poor center). They can be useful for designing ionic liquid crystals. The crystals of the morpholinium-based compounds with sulfosuccinate anions and long alkane chains, C₈ to C₁₈, exhibit hexagonal columnar phases at room temperature.²⁴

Morpholinium-based RTILs are practical in electrolyte applications because of straightforward synthesis, low cost, and high mobility of the lithium cation.²⁵ Lithium interacts

strongly with the oxygen group in the morpholinium-based cation. Such cation–cation interactions draw strong interest in view of electrolyte applications, such as in batteries, solar cells, and supercapacitors. Unfortunately, these RTILs are viscous. They reveal a large electrochemical window in conjunction with reasonable conductivity. According to Galinski and Stepniak, mixtures of the morpholinium-based RTILs with propylene carbonate are prospective electrolytes for electrochemical double-layer capacitors.²⁶ These authors reported temperature dependence of ionic conductivities and electrochemical stabilities of *N*-ethyl-*N*-butylmorpholinium and *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imides in mixtures with propylene carbonate. It was found that the conductivity maximum for these mixtures is located at 20 mol % of RTIL.

An ability of the morpholinium cation to participate in micellization was recently reported.²⁰ The alkyl chain is responsible for an interplay between hydrophobic and hydrophilic interactions determining micellization behavior. Besides that, morpholinium-based RTILs are interesting as prospective catalysts for organic synthesis, heat stabilizers, oxidants, and corrosion inhibitors. Morpholinium-based cations were coupled with tetrafluoroborate, hexafluorophosphate, bis(trifluoromethanesulfonyl)imide, formate, and bromide, as well as with anions decorated with long alkyl chains.²⁴

Domanska and Lukoshko²⁷ measured activity coefficients at infinite dilution for *N*-butyl-*N*-methylmorpholinium tricyano-

Received: May 29, 2015

Revised: June 25, 2015

Published: June 30, 2015

methanide in 61 solvents, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, ethers, ketones, and acetonitrile. As compared to *N*-butyl-*N*-methylpyrrolidinium tricyanomethanide, these RTILs exhibit higher selectivity in separation of aromatic hydrocarbons from aliphatic hydrocarbons. Successful separation of thiophene and pyridine from heptane was highlighted. The demonstrated selectivity toward sulfur and nitrogen-containing compounds is interesting for many prospective applications of ionic liquids.

Halogenation of the morpholinium-based cations has never been reported. This work investigates fluorination and chlorination of the *N*-ethyl-*N*-methylmorpholinium cation from the thermodynamic perspective. We identify five chemically nonequivalent prospective halogenation sites in the *N*-ethyl-*N*-methylmorpholinium cation. Not only was halogenation of the side hydrocarbon chains (ethyl and methyl) considered, but also halogenation of the morpholine ring was investigated. We show that substitutional fluorination is thermodynamically more favorable in all cases. Chlorination is also permitted, but it is ca. 4 times less favorable. These insights were obtained using highly accurate *ab initio* coupled-cluster electronic structure calculations.²⁸ The resulting molecular partition functions were further processed to obtain thermodynamic quantities, such as enthalpy, entropy, free energy of reaction, and their temperature dependence.

METHODOLOGY

Fluorination and chlorination of the *N*-ethyl-*N*-methylmorpholinium cation is investigated from the thermodynamic perspective. The direction of a chemical reaction taking part at constant temperature and constant pressure is determined by evolution of the corresponding Gibbs free energy, $G = f(T, P)$. Gibbs free energy is expressed through a linear combination of enthalpy (H) and entropy (S) as $G = H - TS$, where T stands for temperature in kelvin. We report these functions for the halogenation reactions and their temperature dependence over the temperature range between 200 and 500 K.

The internal energies, enthalpies, entropies, and free energies are derived from the molecular partition function using the equations of statistical mechanics. The partition function is derived from a quantum-chemical calculation and subsequent frequency analysis for a given chemical entity. All thermodynamics quantities computed in this way correspond to an ideal gas. It is important that an electronic structure method used for wave function optimization accounts for electron correlation. This is because major numerical errors arise from lack of electron correlation, even though a reliable equilibrium geometry of the molecule can be obtained at the Hartree–Fock or density functional theory levels.

The electronic structure of all systems was optimized using the coupled-cluster technique.²⁸ Coupled-cluster was born in nuclear physics but received its recognition years later when applied to many-body electronic systems.²⁸ The coupled-cluster technique belongs to the group of post-Hartree–Fock methods. That is, any calculation using the coupled-cluster technique starts with a conventional one-electron calculation; then, the correlation between electrons is accounted for. This method provides very accurate energies of electron levels. Unfortunately, the underlying computational cost is high; thus, consideration of large molecules is prohibited. 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.²⁹

The split-valence triple- ζ 6-311G Pople basis set with added polarization and diffuse functions was applied. All electrons were considered explicitly. The pristine cation contains 72 electrons, the fluorinated cation 80 electrons, and the chlorinated cation 88 electrons. The wave function convergence criterion at every self-consistent field (SCF) step was set to 10^{-8} hartree. The described electronic structure methods are available in the GAMESS simulation suite.³⁰

RESULTS AND DISCUSSION

We selected *N*-ethyl-*N*-methylmorpholinium as a prototypical cation. The shorter hydrocarbon chain is methyl, while the longer chain is ethyl, as it is in the currently available experiments. The terminating methyl group of ethyl is weakly influenced by the morpholine ring. This is also the case in imidazolium- and pyridinium-based RTILs.^{12,31,32} Indeed, this group appears nearly neutral. For this reason, longer hydrocarbon chains can be avoided in simulation to save computational resources. Because morpholinium-based cations are rather new to chemists, widely applied nomenclature of their interaction sites is absent. We propose to apply the following nomenclature to label the symmetrically nonequivalent carbon atoms (Figure 1). C(N) denotes the two carbon atoms linked

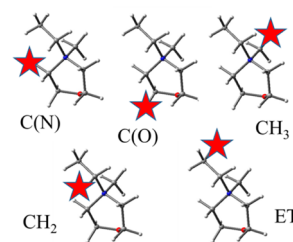


Figure 1. Halogen substitution sites in the *N*-ethyl-*N*-methylmorpholinium cation. Carbon atoms are gray; hydrogen atoms are white; nitrogen atom is blue; oxygen atom is red; and the halogen (fluorine, chlorine) atom is marked with a red star. As was found by quantum-chemical calculations, five symmetrically nonequivalent carbon atoms are available.

to nitrogen, while C(O) denotes the two carbon atoms linked to oxygen. Recall that nitrogen is the most electron-deficient interaction site in this cation, while oxygen is the most electron-rich site. The carbon atoms in the side chains are named as usual: CH₃ for methyl group, CH₂ for methylene group, and ET for the terminating methyl group in the ethyl chain.

The morpholinium-based cation is a significantly different chemical entity, compared to many other previously known RTIL cations, such as imidazolium, pyridinium, piperidinium, pyrrolidinium, tetraalkylammonium, cholinium, etc. All the enumerated cations are monopolar because they contain only a positively charged interaction center. This can be a single center, such as the nitrogen atom in the pyridine ring, or two centers, such as the two nitrogen atoms in the imidazole ring. In turn, the *N*-ethyl-*N*-methylmorpholinium cation contains one positively charged center (nitrogen) and one negatively charged center (oxygen), whereas all other atoms exhibit smaller charges. The electrostatic charge on the nitrogen atom amounts to $+0.29e$. It almost compensates the opposite charge of the oxygen atom, which is equal to $-0.37e$. The two carbon atoms located near oxygen have $+0.19e$, and the two carbon

atoms near nitrogen have $-0.19e$ and $-0.10e$. The symmetry near nitrogen is broken because of the strong influence of the methyl group, which is electron deficient, $+0.16e$. Another difference of the morpholinium cation from most other RTIL cations is that its ring is clearly nonplanar. For instance, the O–C–C–N angle is 32° . The C–O–C angle is 112° , and the C–N–C angle is 108° . Compare these values to an ideal angle of 120° in the planar hexagon, such as benzene. The observations regarding geometry and electron density distribution in the *N*-ethyl-*N*-methylmorpholinium cation are important for understanding of the halogenation trends discussed below.

Figure 2 summarizes the thermodynamic potentials for the fluorination reaction taking place via the five symmetrically

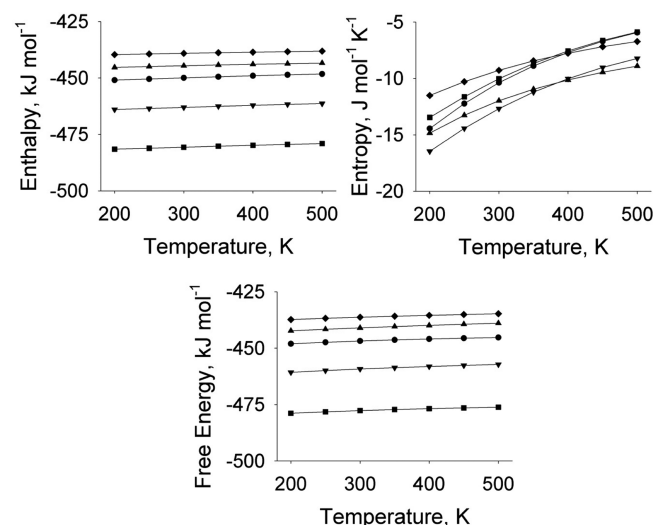


Figure 2. Enthalpy, entropy, and free-energy change during the substitutional fluorination reaction of the *N*-ethyl-*N*-methylmorpholinium cation, which takes place via the C(N) (●), C(O) (■), CH₃ (▲), CH₂ (▼), and ET (◆) reaction sites, see Figure 1.

different sites: C(N), C(O), CH₃, CH₂, and ET. Enthalpy is the decisive factor determining the reaction direction. The difference in enthalpy between the products (C₇H₁₅NOF and HF) and the reactants (C₇H₁₆NO and F₂) is significantly negative, indicating that carbon–fluorine covalent bonds in the morpholine ring are more stable than carbon–hydrogen bonds. Favorable halogenation of the hydrocarbon chains was rather expected from conventional chemical wisdom. Isobaric heat capacities are small. The reactions become slightly less favorable as temperature increases. Entropy changes are negative, that is, the entropy factor prohibits halogenation. However, the calculated entropy factor is too small compared to the enthalpy changes.

The trend in free energy completely repeats the trend in enthalpy. The most favorable fluorination site is C(O). This is not easy to predict without an appropriate numerical analysis because one would rather expect straightforward fluorination of the hydrocarbon chains. It is well-known that hydrocarbons are readily fluorinated in the laboratory synthesis. The easier fluorination via the C(O) site indicates a strong role of the oxygen atom, which pulls electronic density of the adjacent carbon atoms toward itself. Having attained partially positive charges, the C(O) carbon atoms react with fluorine, which is strongly electronegative. More polar covalent bonds are formed. The same reasoning applies to the methylene group site, which is ca. 10 kJ mol^{−1} less favorable. The differences

between the remaining interaction sites are smaller, although they still exceed kT .

Chlorination also appears favorable for all the perspective reaction sites. However, the free-energy gain (Figure 3) is ca. 4

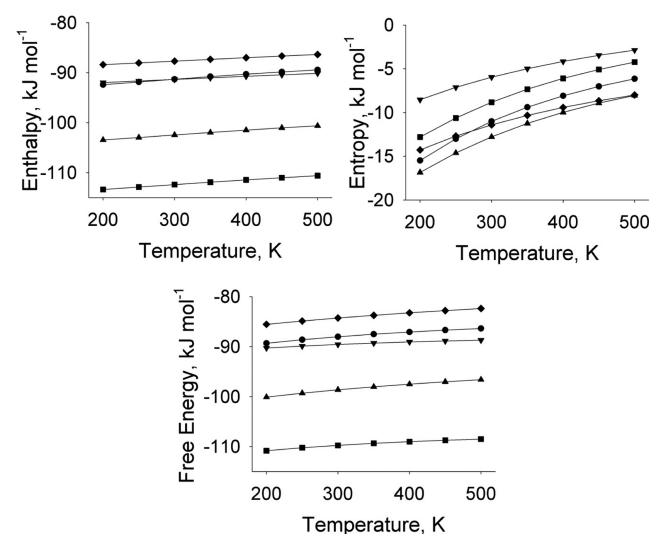


Figure 3. Enthalpy, entropy, and free-energy change during the substitutional chlorination reaction of the *N*-ethyl-*N*-methylmorpholinium cation, which takes place via the C(N) (●), C(O) (■), CH₃ (▲), CH₂ (▼), and ET (◆) reaction sites, see Figure 1.

times smaller than that in the case of fluorination. This may be due to weaker carbon–chlorine bonds and also, to a certain extent, to steric hindrances. The chlorine atom is significantly larger than the fluorine atom. Similar to fluorination, the C(O) site is most easily chlorinated, and the terminal atom of the ethyl chain is relatively resistant to this reaction. Chlorination of the methyl group is easier than chlorination of the methylene group, although it was the opposite in the case of fluorination. It is probable that because of its size, the chlorine atom perturbs geometry of this part of the *N*-ethyl-*N*-methylmorpholinium cation.

Analysis of electrostatic charges on the fluorine and chlorine atoms (Figures 4 and 5) is helpful in understanding the thermodynamic observations and trends. The fluorine atom is negative in all positions of the reaction product. This is expected because of a high electron affinity of this element. However, prediction of particular values was challenging. As discussed above, the C(O) site indeed favors the largest negative electronic charge of fluorine because of proximity to another electronegative atom, oxygen. The terminal methyl group of the ethyl chain is close to neutrality, $q = +0.05e$, in the pristine morpholinium cation. The fluorine atom makes it electron-deficient, $q = +0.13e$, by inducing an unusually large positive charge on the carbon atom, $q = +0.32e$. This makes fluorination reaction at this site less favorable, according to Figure 2.

The chlorine atom can be both positively and negatively charged, although these charges are small. Note that a positive charge on chlorine in the morpholinium cation is favored by the fact that the overall structure must maintain the $+1e$ charge. If two atoms with different electronegativities are bonded, it does not implicitly mean that one of them will be necessarily electron-deficient and the other one will be electron-rich. Both can be positively charged (with different charges according to

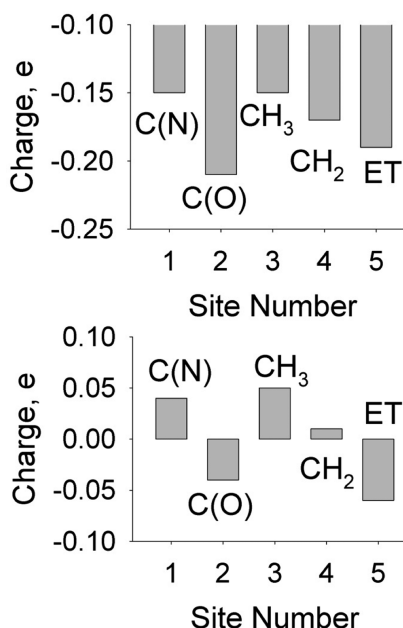


Figure 4. Electrostatic potential fitted charge on the fluorine (top panel) and chlorine (bottom panel) atoms in the *N*-ethyl-*N*-methylmorpholinium cation in the five investigated positions: C(N), C(O), CH₃, CH₂, and ET, see Figure 1. Charges on the carbon atoms are provided in the discussion, where applicable.

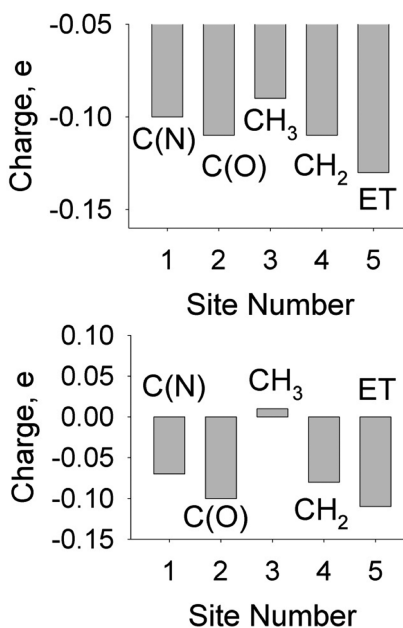


Figure 5. Mulliken charge on the fluorine (top panel) and chlorine (bottom panel) atoms in the morpholinium cation in the five investigated positions: C(N), C(O), CH₃, CH₂, and ET, see Figure 1. Charges on the carbon atoms are provided in the discussion, where applicable.

electronegativity) depending on their particular position in the ion structure.

Mulliken charges are derived directly from the optimized wave function. They represent a convenient measure of the electron population at a given atom, although their absolute values are not recommended as a characteristic of electrostatic interactions. It is interesting to note that chlorine in the methyl group, CH₂Cl, has a small, but positive charge. The

chlorination at CH₃ is relatively favorable, being inferior only to the chlorination at the C(O) site. In turn, fluorination at CH₃ is less favorable, likely because fluorine cannot acquire a positive charge. The methyl group is electron deficient, $q = +0.21e$. This partial charge is important in maintaining the total $+1e$ charge on the cation. Attachment of fluorine necessitates redistribution of the electron density over the entire *N*-ethyl-*N*-methylmorpholinium cation.

It must be noted that our results were obtained under an ideal gas approximation. That is, no ion–molecular interactions were considered and no solvation effects or steric hindrances were accounted for. Furthermore, excited states were not considered. This should be a valid approximation for ionic liquids, in which highest occupied molecular orbital–lowest unoccupied molecular orbital gaps are significant.

CONCLUDING REMARKS

The present work reports, for the first time, a theoretical study of the fluorination and chlorination reactions of the prototypical morpholinium cation used in RTILs. Thermodynamic potentials of all reactions are discussed in relationship to the electronic structure and geometry of the cation. We show that halogenation of the cation is energetically favorable in all considered cases. Most likely, the described ionic derivatives will be soon synthesized starting from the morpholinium-based cations and using the well-established methods for fluorination (e.g., treatment by potassium fluoride) and chlorination (e.g., treatment by gaseous chlorine). Fluorination brings a larger free-energy gain.

Substitution of hydrogen atoms by halogen atoms is an important tool in tuning physical-chemical properties of ionic liquids. Unlike hydrogen, fluorine and chlorine are unable to maintain hydrogen bonding with the counterion and polar solvent molecules, if any are present. Hydrogen bonding is an important phenomenon determining identity of many RTILs. Its presence is favorable for certain applications, but it is unfavorable for other applications. Furthermore, fluorination is expected to lead to more polar bonds, i.e., higher partial charges at the corresponding interaction centers. Halogenation is an important tool in tuning hydrophobicity–hydrophilicity balance of RTILs. Understanding of halogenation regularities is necessary for future progress in the field of RTILs, while relatively little has been performed in this direction thus far.

The reported simulations of chemical thermodynamics encourage experimental efforts in organic chemistry and provide guidance for further development of RTILs. The fluorinated and chlorinated morpholinium-based cations are expected to exhibit physical-chemical properties significantly different than those of the original cations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vvchaban@gmail.com. Tel: +55 12 3309-9573. Fax: +55 12 3921-8857.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was partially funded by CAPES (Brazil). O.V.P. acknowledges financial support of the U.S. National Science Foundation, Grant CHE-1300118.

■ REFERENCES

- (1) Chaban, V. V.; Prezhdo, O. V. Ionic and Molecular Liquids: Working Together for Robust Engineering. *J. Phys. Chem. Lett.* **2013**, *4*, 1423–1431.
- (2) Patel, R.; Kumari, M.; Khan, A. B. Recent Advances in the Applications of Ionic Liquids in Protein Stability and Activity: A Review. *Appl. Biochem. Biotechnol.* **2014**, *172*, 3701–3720.
- (3) Guo, F.; Zhang, S. J.; Wang, J. J.; Teng, B. T.; Zhang, T. Y.; Fan, M. H. Synthesis and Applications of Ionic Liquids in Clean Energy and Environment: A Review. *Curr. Org. Chem.* **2014**, *19*, 455–468.
- (4) Pandey, S. Analytical Applications of Room-Temperature Ionic Liquids: A Review of Recent Efforts. *Anal. Chim. Acta* **2006**, *556*, 38–45.
- (5) Kaintz, A.; Baker, G.; Benesi, A.; Maroncelli, M. Solute Diffusion in Ionic Liquids, Nmr Measurements and Comparisons to Conventional Solvents. *J. Phys. Chem. B* **2013**, *117*, 11697–11708.
- (6) Chaban, V. Hydrogen Fluoride Capture by Imidazolium Acetate Ionic Liquid. *Chem. Phys. Lett.* **2015**, *625*, 110–115.
- (7) Bica, K.; Deetlefs, M.; Schroder, C.; Seddon, K. R. Polarisabilities of Alkylimidazolium Ionic Liquids. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2703–2711.
- (8) Emel'yanenko, V. N.; Zaitsau, D. H.; Verevkin, S. P.; Heintz, A.; Voss, K.; Schulz, A. Vaporization and Formation Enthalpies of 1-Alkyl-3-Methylimidazolium Tricyanomethanides. *J. Phys. Chem. B* **2011**, *115*, 11712–11717.
- (9) Chaban, V. V.; Prezhdo, O. V. How Toxic Are Ionic Liquid/Acetonitrile Mixtures? *J. Phys. Chem. Lett.* **2011**, *2*, 2499–2503.
- (10) Xu, C. H.; Margulis, C. J. Solvation of an Excess Electron in Pyrrolidinium Dicyanamide Based Ionic Liquids. *J. Phys. Chem. B* **2015**, *119*, 532–542.
- (11) Li, H.; Endres, F.; Atkin, R. Effect of Alkyl Chain Length and Anion Species on the Interfacial Nanostructure of Ionic Liquids at the Au(111)-Ionic Liquid Interface as a Function of Potential. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14624–14633.
- (12) Chaban, V. V.; Voroshylova, I. V.; Kalugin, O. N.; Prezhdo, O. V. Acetonitrile Boosts Conductivity of Imidazolium Ionic Liquids. *J. Phys. Chem. B* **2012**, *116*, 7719–7727.
- (13) Niedermeyer, H.; Ab Rani, M. A.; Lickiss, P. D.; Hallett, J. P.; Welton, T.; White, A. J. P.; Hunt, P. A. Understanding Siloxane Functionalised Ionic Liquids. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2018–2029.
- (14) Castner, E. W.; Margulis, C. J.; Maroncelli, M.; Wishart, J. F. Ionic Liquids: Structure and Photochemical Reactions. *Annu. Rev. Phys. Chem.* **2011**, *62*, 85–105.
- (15) Keskin, S.; Kayrak-Talay, D.; Akman, U.; Hortacsu, O. A Review of Ionic Liquids Towards Supercritical Fluid Applications. *J. Supercrit. Fluids* **2007**, *43*, 150–180.
- (16) Silvester, D. S.; Compton, R. G. Electrochemistry in Room Temperature Ionic Liquids: A Review and Some Possible Applications. *Z. Phys. Chem.* **2006**, *220*, 1247–1274.
- (17) Shamsuri, A. A.; Daik, R. Applications of Ionic Liquids and Their Mixtures for Preparation of Advanced Polymer Blends and Composites: A Short Review. *Rev. Adv. Mater. Sci.* **2015**, *40*, 45–59.
- (18) Fileti, E. E.; Chaban, V. V. Imidazolium Ionic Liquid Helps to Disperse Fullerenes in Water. *J. Phys. Chem. Lett.* **2014**, *5*, 1795–1800.
- (19) Hantal, G.; Voroshylova, I.; Cordeiro, M. N. D. S.; Jorge, M. A. Systematic Molecular Simulation Study of Ionic Liquid Surfaces Using Intrinsic Analysis Methods. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5200–5213.
- (20) Kamboj, R.; Bharmoria, P.; Chauhan, V.; Singh, S.; Kumar, A.; Mithu, V. S.; Kang, T. S. Micellization Behavior of Morpholinium-Based Amide-Functionalized Ionic Liquids in Aqueous Media. *Langmuir* **2014**, *30*, 9920–9930.
- (21) Brigouleix, C.; Anouti, M.; Jacquemin, J.; Caillon-Caravanier, M.; Galiano, H.; Lemordant, D. Physicochemical Characterization of Morpholinium Cation Based Protic Ionic Liquids Used as Electrolytes. *J. Phys. Chem. B* **2010**, *114*, 1757–1766.
- (22) Yue, C. B. Aromatic Compounds Mannich Reaction Using Economical Acidic Ionic Liquids Based on Morpholinium Salts as Dual Solvent-Catalysts. *Synth. Commun.* **2010**, *40*, 3640–3647.
- (23) Zhang, Q. S.; Liu, A. X.; Guo, B. N.; Wu, F. Synthesis of Ionic Liquids Based on the N-Methyl-N-Allyl Morpholinium Cation. *Chem. J. Chin. Univ.* **2005**, *26*, 340–342.
- (24) Lava, K.; Binnemans, K.; Cardinaels, T. Piperidinium, Piperazinium and Morpholinium Ionic Liquid Crystals. *J. Phys. Chem. B* **2009**, *113*, 9506–9511.
- (25) Yeon, S. H.; Kim, K. S.; Choi, S.; Lee, H.; Kim, H. S.; Kim, H. Physical and Electrochemical Properties of 1-(2-Hydroxyethyl)-3-Methyl Imidazolium and N-(2-Hydroxyethyl)-N-Methyl Morpholinium Ionic Liquids. *Electrochim. Acta* **2005**, *50*, 5399–5407.
- (26) Galinski, M.; Stepniak, I. Morpholinium-Based Ionic Liquid Mixtures as Electrolytes in Electrochemical Double Layer Capacitors. *J. Appl. Electrochem.* **2009**, *39*, 1949–1953.
- (27) Domanska, U.; Lukoshko, E. V. Thermodynamics and Activity Coefficients at Infinite Dilution for Organic Solutes and Water in the Ionic Liquid 1-Butyl-1-Methylmorpholinium Tricyanomethanide. *J. Chem. Thermodyn.* **2014**, *68*, 53–59.
- (28) Cizek, J. Origins of Coupled-cluster Technique for Atoms and Molecules. *Theoretica Chimica Acta* **1991**, *80*, 91–94.
- (29) Pople, J. A.; Headgordon, M.; Raghavachari, K. Quadratic Configuration-Interaction - a General Technique for Determining Electron Correlation Energies. *J. Chem. Phys.* **1987**, *87*, 5968–5975.
- (30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; et al. General Atomic and Molecular Electronic-Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (31) Chaban, V. V.; Prezhdo, O. V. Polarization Versus Temperature in Pyrrolidinium Ionic Liquids. *J. Phys. Chem. B* **2014**, *118*, 13940–13945.
- (32) Chaban, V. Competitive Solvation of the Imidazolium Cation by Water and Methanol. *Chem. Phys. Lett.* **2015**, *623*, 76–81.