# Halogenation Thermodynamics of Pyrrolidinium-Based Ionic Liquids

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ABSTRACT: Room-temperature ionic liquids (RTILs) exhibit a large difference between melting and boiling points. They are highly tunable thanks to numerous accessible combinations of the cation and the anion. On top of that, cations can be functionalized using methods of organic chemistry. This paper reports gas-phase thermodynamics (enthalpy, entropy, and Gibbs free energy) of the halogenation reactions (fluorination, chlorination, bromination) involving protonated pyrrolidine $C_4H_{10}N^+$, protic N-ethylpyrrolidinium $C_4H_9N(C_2H_5)^+$, and aprotic N-ethyl-N-methylpyrrolidinium $C_4H_8N(CH_3)(C_2H_5)^+$ cations. Substitution of all symmetrically nonequivalent hydrogen atoms was compared based of the thermodynamic favorability. Fluorination of all sites is much more favorable than chlorination, whereas chlorination is somewhat more favorable than bromination. This is not trivial, because electronegative fluorine and chlorine have to compete for the already insufficient number of electrons with other atoms belonging to the pyrrolidinium-based cations. The difference between different reaction sites within the cations is modest, although it often exceeds kT at simulated temperatures. The correlation between thermodynamics and electronic density distribution has been established, which allows new simple prediction of the reaction pathways. The reported results inspire further chemical modifications of the pyrrolidinium-based RTILs to achieve ever finer tunability of physical chemical properties.
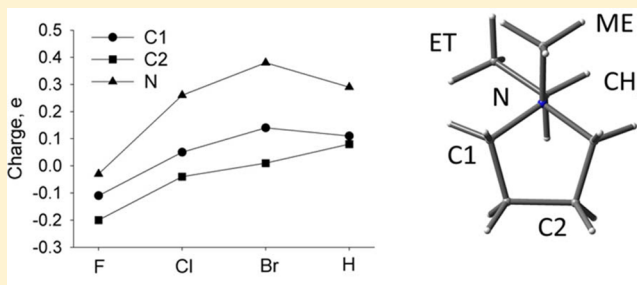
INTRODUCTION

Room-temperature ionic liquids (RTILs) constitute a large and permanently growing class of chemical compounds, which are based on the organic cation and organic or inorganic anion.[1−15] With just a few exceptions, the cations of RTILs are typically based on a nitrogen-containing heterocycle, where the nitrogen atom is primarily responsible for a deficient electron density. It should be understood, however, that many of the discussed cations retain aromatic nature of the corresponding heterocycles, which implies delocalized valence electrons. That is why no atom in the RTIL cation carries a charge of +1e, while most atoms are slightly electron deficient. Together with asymmetry thanks to the grafted hydrocarbon chains, this feature explains why ionic liquids differ from conventional inorganic salts so drastically. Anions of RTILs are less tunable if they are inorganic, such as tetrafluoroborate, hexafluorophosphate, dicyanamide, tricyanomethanide, chloride, bromide, and so forth. If the anion is organic, it can be modified using the same synthetic approaches as in the case of the cation.

Ionic liquids can be both protic and aprotic. Protic RTILs represent a broad and promising subclass of compounds.[16,17] They have long been used as sources of a highly basic chloride anion for spectroscopic studies and to obtain salt mixtures with low melting temperatures. A large group of protic RTILs with benign and edible cations and biologically interesting anions is available. Ohno and co-workers[18] reported a large number of protic ionic liquids. These researchers used proton transfer from hydrogen bis(trimethylsulfonyl)imide, the conjugate basis of which is an anion, which is known to be responsible for low melting points. In general, melting points and glass transition temperatures appear lower for protic RTILs than for similar aprotic RTILs. Consequently, ionic conductivity of protic RTILs is also higher (consider, for example, ethylammonium nitrate[19,20]), which may be important for their fuel cell applications[21,22] in conjunction with proper cosolvents. Protic RTILs exhibit extensive possibilities to engender hydrogen bonding networks in the condensed phases.

Pyrrolidinine or tetrahydropyrrole, C_4H_9N, can be viewed as a cyclic amine with four carbon atoms in the cycle. This is a transparent liquid with a smell of ammonia. The pyrrolidine fragment is widely represented in natural compounds. Pyrrolidine can be protonated in the acidic environments to provide $C_4H_{10}N^+$. $C_4H_{10}N^+$ is a building block for an emerging class of the pyrrolidinium-based RTILs. This charged compound can be stabilized by grafting hydrocarbon chains in place of hydrogen atoms, that is, $C_4H_8NH_2^+ \rightarrow C_4H_{10}N(CH_3)(C_2H_5)^+$. Coupling of $C_4H_{10}N(CH_3)(C_2H_5)^+$ with a suitable anion provides a new RTIL. Research attention to this class of RTILs is yet insufficient,[23−32] as compared to imidazolium- and pyridinium-based RTILs.[2,10,13,33−35]

Halogenated derivatives are omnipresent in the organic synthesis, both as the end-products and in the numerous established methods for total synthesis. Fluorine, chlorine, and bromine atoms, when substituting hydrogen in the organic molecules, change chemical and physical chemical properties significantly and sometimes drastically.[36−38] Many widely

applied organic solvents were obtained by halogenating aliphatic hydrocarbons (gases). Modification of RTILs using halogenation is interesting for a few reasons: (1) more available solvents with slightly variable sets of properties approach an era of task-specific ionic liquids; (2) halogen atoms are able to block specific binding sites and promote additional binding sites; (3) more electronegative atoms, as compared to hydrogen, induce novel charge density distributions within a cation.

This work reports an accurate gas-phase thermodynamics (enthalpy, entropy, and free energy) of fluorination, chlorination, and bromination of the three pyrrolidinium-based cations, $C_4H_{10}N^+$, protic N-ethylpyrrolidinium $C_4H_9N(C_2H_5)^+$, and aprotic N-ethyl-N-methylpyrrolidinium $C_4H_8N(CH_3)(C_2H_5)^+$. The below discussion is devoted to atomistic-precision interpretation of why some reaction sites are more favorable and other sites are less favorable. The correlation scheme involving partial electrostatic charges has been established, which allows for cheaply predicting more preferable halogenation sites without costly free energy calculations.

METHODOLOGY

Thermodynamics of fluorination, chlorination, and bromination of the N-ethyl-N-methylpyrrolidinium cation was investigated. The direction of the halogenation reaction taking part at constant temperature and constant pressure is determined by an evolution of the Gibbs free energy, $G = f(T,P)$, over reaction stages. The Gibbs free energy is expressed through a linear combination of enthalpy (H) and entropy (S) as $G = H - TS$, where T is an absolute temperature. This paper reports enthalpy, entropy, and the Gibbs free energy for the substitution reactions EM-PYRR + Hal_2 = EM-PYR(Hal) + HHal between 200 and 500 K.

The results were derived from molecular partition functions using the established equations of statistical mechanics. Wave function optimization followed by geometry optimization, where necessary, was supplemented by computation of force constants and corresponding vibrational frequencies. Vibrational frequencies constitute second derivatives of energy with respect to mass-weighted atomic coordinates. The harmonic oscillator behavior was assumed. The wave function must be optimized at a high level of theory, because electron correlation is responsible for accurate thermodynamic potentials. The coupled-cluster theory[39] was used in this work as an electronic structure method. A calculation employing the coupled-cluster technique starts with a conventional one-electron self-consistent field procedure. Afterward, correlation between electrons is accounted for. The implementation of the coupled-cluster theory employed in the present work uses single and double substitutions from the Hartree−Fock determinant. Furthermore, it includes triple excitations non-iteratively.[40] The split-valence triple-ζ 6-311G Pople basis set with added polarization and diffuse functions to all atoms was applied (the Gaussian-type notation is 6-311++G**). This basis set is sufficiently large to produce accurate energies. Trial comparisons with somewhat larger and smaller basis sets did not identify systematic discrepancies. All electrons were considered explicitly. The wave function energy convergence criterion at every self-consistent field step was set to 10^{-8} Hartree. The global minimum of each structure was located following the well-established basin hopping algorithm.[41] Partial charges were calculated by fitting electrostatic potential,

as described previously.[42] The described electronic structure methods are available in the GAMESS simulation suite.[43]

RESULTS AND DISCUSSION

We considered three pyrrolidinium-based cations, as depicted in Figure 1, to observe and investigate different halogenation
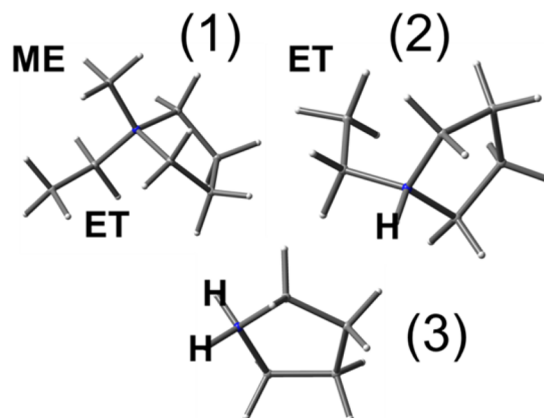

Figure 1. Three pyrrolidinium-based cations investigated in the present work: (1) N-ethyl-N-methylpyrrolidinium $C_4H_8N(CH_3)$-$(C_2H_5)^+$; (2) protic N-ethylpyrrolidinium $C_4H_9N(C_2H_5)^+$; and (3) protonated pyrrolidine $C_4H_{10}N^+$.
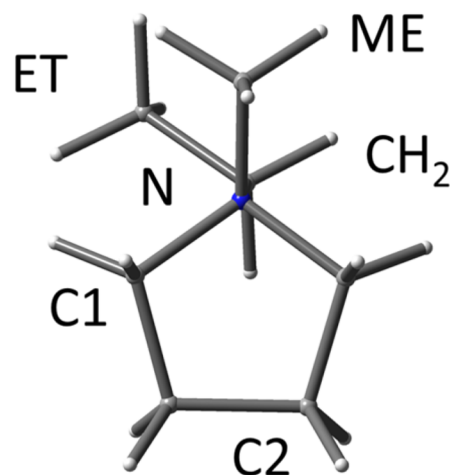

Figure 2. Designation of the reaction sites of the N-ethyl-N-methylpyrrolidinium cation. The reaction sites of the protic N-ethylpyrrolidinium and protonated pyrrolidine use the same names, where applicable.

sites. First, the six sites (Figure 2) of the N-ethyl-N-methylpyrrolidinium cation were studied (Tables 1−3). "C1" stands for the two carbon atoms of the ring bound to the nitrogen, "N", atom; "C2" stands for the two carbon atoms of the ring, which are not bound to N; ":ME" and "ET" are the terminal sp³ carbon atoms of the methyl and ethyl chains, respectively. "CH₂" is the methylene group of the ethyl chain. Second, the methyl chain was removed to obtain the N-ethylpyrrolidinium, a protic cation. The corresponding proton at the N site is also able to participate in the substitution reactions. Third, the positively charged pyrrolidinium moiety

Table 1. Standard Thermodynamic Potentials for the Fluorination Reaction of the *N*-ethyl-*N*-Methylpyrrolidinium and *N*-ethylpyrrolidinium (See the N Site) Cations at Standard Conditions

site	enthalpy, kJ mol^{-1}	entropy, J mol^{-1} K^{-1}	free energy, kJ mol^{-1}
C1	−462	−16.6	−457
C2	−463	−18.7	−458
N	−287	+8.5	−289
ME	−446	−15.7	−441
CH$_2$	−467	−18.0	−462
ET	−442	−12.8	−438

Table 2. Standard Thermodynamic Potentials for the Chlorination Reaction of the *N*-ethyl-*N*-Methylpyrrolidinium and *N*-Ethylpyrrolidinium (See the N Site) Cations at Standard Conditions

site	enthalpy, kJ mol^{-1}	entropy, J mol^{-1} K^{-1}	free energy, kJ mol^{-1}
C1	−96.2	−16.4	−91.3
C2	−114	−17.7	−109
N	−7.60	+4.57	−9.02
ME	−90.2	−5.24	−88.6
CH$_2$	−106	−19.5	−99.9
ET	−95.6	−14.1	−91.4

Table 3. Standard Thermodynamic Potentials for the Bromination Reaction of the *N*-ethyl-*N*-Methylpyrrolidinium and *N*-Ethylpyrrolidinium (See the N Site) Cations at Standard Conditions

site	enthalpy, kJ mol^{-1}	entropy, J mol^{-1} K^{-1}	free energy, kJ mol^{-1}
C1	−22.9	−18.1	−17.5
C2	−43.3	−14.7	−38.9
N	+41.1	+4.71	+39.7
ME	−21.8	−15.9	−16.9
CH$_2$	−31.7	−19.7	−25.8
ET	−24.8	−13.8	−20.7

without hydrocarbon chains, $C_4H_{10}N^+$ (protonated pyrrolidine), was considered. The three supposedly different reaction sites, C1, C2, and N, were investigated (Table 4) in $C_4H_{10}N^+$.

Gibbs free energy change is responsible for the direction of the process at constant temperature and pressure. A negative Gibbs energy of a reaction does not, however, necessarily mean

Table 4. Standard Thermodynamic Potentials for Fluorination, Chlorination, and Bromination of $C_4H_{10}N^+$ at Standard Conditions

site	enthalpy, kJ mol^{-1}	entropy, J mol^{-1} K^{-1}	free energy, kJ mol^{-1}
		Fluorination	
C1	−267	−3.40	−266
C2	−480	+11.5	−483
N	−481	+12.3	−485
		Chlorination	
C1	+2.50	+35.2	−8.05
C2	−122.8	+18.8	−128
N	−134.6	+13.1	−139
		Bromination	
C1	+46.0	+16.5	+41.1
C2	−29.0	−10.5	−25.9
N	−64.2	+14.7	−68.6

that a reaction occurs under given conditions, because certain stages can be kinetically forbidden. Nevertheless, a negative Gibbs free energy change does mean that products are more stable than reactants. Consequently, the corresponding reaction can always be performed using this or that transformation pathway. Thermodynamic data are of high importance for synthetic chemistry, because they allow to (1) understand possible products, byproducts, and intermediates; (2) find out a thermal effect of the reaction; and (3) identify the most probable reaction sites in cases where a reactant contains a number of similar reaction sites. This knowledge defends undesirable reaction sites prior to functionalization of an entire molecule.

Simulation of chemical reactions in real-time is impossible at the present stage of development of computational science. Exceptions to this rule are rare and include only reactions with very low activation barriers and very negative free energy alterations. Certain slower reactions can be described using reactive force fields, which are, unfortunately, available for quite a limited set of compounds. Such simulations must be done at high temperatures (1000−3000 K) to make a reaction happen over an observable time interval, usually not exceeding a nanosecond. In this context, thermodynamic analysis brings a lot of important results, which are helpful for chemists.

This work summarizes thermodynamic potentials for a large number of halogenation (fluorination, chlorination, and bromination) reactions involving the pyrrolidinium-based cations. Halogenation of ionic liquids is a very interesting transformation because it achieves significantly different physical chemical properties. For instance, hydrogen bonding, if any, of the cation with the anion or polar molecular cosolvent can be abandoned by elimination of the corresponding hydrogen atom. Furthermore, an electron density can be redistributed fostering formation of new reaction sites. The pyrrolidinium-based cations contain a significant number of possible halogenation sites, C1, C2, N, Me, ET, CH$_2$. While it can be generally anticipated that halogenation at any of these sites is thermodynamically favorable and it likely becomes less favorable when going from molecular fluorine to molecular bromine as a reactant, a mutual relationship of these sites is unclear. Knowledge and thoughtful prediction of this relationship are important to predict reaction products upon halogenation.

According to the ab initio calculations performed in the present work, fluorination of all cations is significantly more favorable than chlorination, while chlorination is systematically more favorable than bromination (Tables 1−4). Almost all halogenation reactions are thermodynamically allowed. The only two exceptions are bromination of the N site of the *N*-ethylpyrridinium cation (+39.7 kJ mol^{-1}) and bromination of the C1 site of the protonated pyrrolidine (+41.1 kJ mol^{-1}). Fluorination and chlorination are favorable irrespective of the reaction site. Interestingly, substitution of one hydrogen atom in the −NH$_2$− group by one bromine atom is thermodynamically permitted (−68.6 kJ mol^{-1}). One must conclude that the ethyl chain creates a steric hindrance for the corresponding substitution reaction to take place. This information is nonintuitive and important for projecting chemical syntheses. Likely, the size of the bromine substituent is too large to seamlessly occupy space in the vicinity of the two carbon atoms and the nitrogen atom.

Entropic contribution to halogenation is negative in most cases. Decrease of entropy does not favor a direct reaction. It

should be kept in mind, however, that $-T \times S$ is marginal as compared to the contribution of enthalpy (Figure 3). In
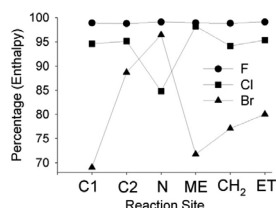

Figure 3. Enthalpy contributions, $x(H)$, to the Gibbs free energy for the halogenation reactions at standard conditions depending on the reaction site. The contributions of entropic factor ($T \times S$) are, consequently, $[100 - x(H)]\%$. Circles correspond to fluorination, squares correspond to chlorination, and triangles correspond to bromination.

comparison, the maximum entropic contribution in the case of fluorination amounts to 1.3% (the C2 site). This contribution increases somewhat for chlorination (5–15%) and additionally increases for bromination (4–31%). Nevertheless, in all considered cases the enthalpy change dominates the chemical transformation. The reported results suggest that chlorination and fluorination can be with a significant accuracy considered using only the enthalpy change. This observation is important because computation of enthalpy is systematically cheaper than computation of the Gibbs free energy. Furthermore, enthalpy contributions are less prone to errors than entropic ones.

The observed increase of the entropic impact in the row F < Cl < Br is natural. It correlates well with weakening of the bond strength in the row C–F > C–Cl > C–Br. Entropy must be considered in the case of reactions (physical chemical processes) where an enthalpy alteration is modest. Indeed, the bromination reaction is only slightly thermodynamically favorable. The energy changes (Table 3) exceed the $k \times T$ product, however.

It is interesting to note that differences exist between the analogous reaction sites in *N*-ethyl-*N*-methylpyrrolidinium, *N*-ethylpyrrolidinium (protic cation), and protonated pyrrolidine. For instance, attachment of a halogen atom to the nitrogen atom of the pyrrolidine ring appears clearly more favorable than at the alternative positions if the alkyl chains (methyl and ethyl) are absent. Considering bromination as an example, $[H-N(C_4H_8)-H]^+ + Br_2 = [H-N(C_4H_8)-Br]^+ + HBr$ brings 68.6 kJ mol^{-1}. In turn, $[C_2H_5-N(C_4H_8)-H]^+ + Br_2 = [C_2H_5-N(C_4H_8)-Br]^+ + HBr$ costs 39.7 kJ mol^{-1}. Reactions at other sites are also thermodynamically different. Fluorination at C1 of $C_4H_{10}N^+$ brings only 266 kJ mol^{-1}, which is over 1.7 times less than it is brought by fluorination at the same site of *N*-ethyl-*N*-methylpyrrolidinium cation (458 kJ mol^{-1}). The general conclusion is that halogenation of the carbon atoms of the pyrrolidine ring with the N-grafted hydrocarbon chains is more favorable. Contrary to that, halogenation of the nitrogen atom appears more favorable when the hydrocarbon chains are absent.

The thermodynamics of the considered reactions is weakly dependent on temperature (Table 5). All isobaric heat capacities, C_p, are small by absolute value and their dependence on the reaction site and the reactant is not pronounced. C_p for the N site is larger than C_p for other sites. It decays from fluorine to bromine (154 to 106 J kg^{-1} K^{-1}) but this trend is not observed when the values are given per mole. Small C_p indicates an insignificant impact of temperature on halogen-

Table 5. Isobaric Heat Capacities of the Fluorination, Chlorination, and Bromination Reactions[a]

site	C_p (fluorination)	C_p (chlorination)	C_p (bromination)
	J mol^{-1} K^{-1}		
C1	8.32	9.60	9.09
C2	8.23	8.31	8.29
N	20.4	20.7	20.5
ME	6.13	7.15	6.79
CH$_2$	8.54	9.08	8.89
ET	4.64	5.37	5.32
	J kg^{-1} K^{-1}		
C1	62.9	64.6	47.1
C2	62.3	55.9	42.9
N	154	139	106
ME	46.3	48.1	35.2
CH$_2$"	64.6	61.1	46.0
ET	35.1	36.1	27.6

[a]These values were derived from the thermodynamic calculations within 200–500 K.

ation, irrespective of the reaction site. Influence of pressure is not considered because reactions take place in the condensed phase compressibility of which can be safely neglected.

One of the most important results of this work is that the C1, C2, N, ME, ET, and CH$_2$ reaction sites of the pyrrolidinium-based cations are not thermodynamically equivalent. Although the found difference is inferior to the difference due to different halogen molecules, it still exceeds the $k \times T$ product in many cases. This means that certain order of halogenation must be expected. Programmed partial halogenation is possible. The products of the reactions will contain a mixture in which fluorine, chlorine, and bromine atoms substitute hydrogen atoms at different positions, both in the pyrrolidine ring and in the side hydrocarbon chains. Such information must be available to synthetic chemists to thoughtfully plan transformations with a particular pyrrolidinium derivative in mind. The discussed modifications of the cations are able to impose significant alterations on the nonbonded interactions within pyrrolidinium-based RTILs and therefore to further tune their physical chemical properties.

The reasons why some halogenation sites are more preferable than others may be complicated to understand even though the entropic contribution of these reactions is modest. In the following, discussion of the reaction sites is performed in light of partial electrostatic charges. Redistribution of an electron density over the cation upon a chemical reaction is a fundamental factor determining the free energy gain. The partial charges (Figure 4) are, in most cases, enough to understand the recorded trends in thermodynamics (Tables 1–4). Recall that the Pauling-scale electronegativity decays in the row F (4.0) > Cl (3.0) > Br (2.8) > H (2.1). Knowing that electronegativity of carbon (2.5) is also important because all of these atoms are bound to carbon in the pyrrolidinium-based cations. Fluorine is always negatively charged, chlorine is nearly neutral, |q| > 0.1e, bromine is always electron deficient, even though its electronegativity exceeds that of carbon. This represents a good illustration that electronegativity as a physical property is of predominantly qualitative nature, which suits best for binary compounds.

The partial electrostatic charges help to understand relations between free energies of reactions. For instance, substitution of the hydrogen atom by a halogen atom at C1 is somewhat less
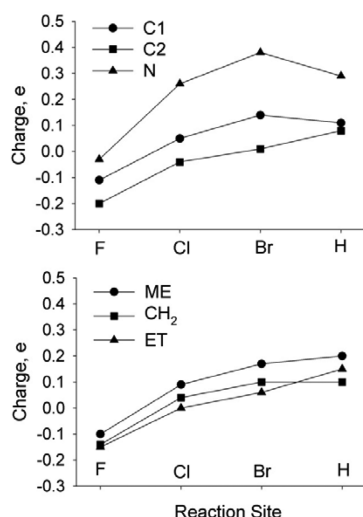
Figure 4. Electrostatic charges of the atoms (F, Cl, Br, and H) participating in the halogenation reactions in their respective positions in the pyrrolidinium-based cations.

favorable, as compared to C2. According to Figure 4, the halogen atoms are allowed to maintain a more negative charge at this site. This is in line with their higher electronegativity and therefore the corresponding reaction sites are more energetically favorable. The C2 reaction site is most distant from the center of the positive charge of the pyrrolidinium-based cations. Therefore, it owns more electron density, which is, upon a reaction, transferred to fluorine, chlorine, and bromine in each respective case. Within the *N*-ethylpyrrolidinium cation (protic), the N site is least favorable, although the halogenation reaction at this site is energetically permitted in the temperature range between 200 and 500 K and atmospheric pressure, except the case of bromination. Indeed, the analysis of partial charges shows that halogen atom must be electron-deficient at this position. Even the fluorine atom is nearly neutral in $[(C_4H_9)(C_2H_5)N{-}F]^+$, whereas chlorine and bromine atoms are clearly positively charged. Interestingly, Table 3 shows a different trend for the case of protonated pyrrolidine. This is again in concordance with the proposed correlation scheme, because the nitrogen atom is negatively charged, $q = -0.18e$, in $C_4H_{10}N^+$. The overall positive charge of this ion is achieved due to the two hydrogen atoms, $q(H) = +0.28e$ each, which are bound to the nitrogen atom. When one of these hydrogen atoms of substituted by the methyl chain, a significant amount of the positive charge appear at ME. That is ME is the least preferable site in the *N*-ethyl-*N*-methylpyrrolidinium cation. Many similar correlations can be found using Tables 1−4 and Figure 4, which are left as an exercise for an interested reader. Alternative descriptors can also be systematically tested, for instance, Taft's polar and steric substituent constants, as exemplified in the recent study of aza-Diels−Alder reactions.[44]

CONCLUDING REMARKS

Thermodynamics of fluorination, chlorination, and bromination is reported and discussed. It was found that halogenation of the *N*-ethyl-*N*-methylpyrrolidinium, *N*-ethylpyrrolidinium, and protonated pyrrolidine cations is thermodynamically allowed in almost all cases. Fluorination is systematically more favorable then chlorination. In turn, chlorination is somewhat more favorable than bromination. This trend originates from the strength of C−F, C−Cl, and C−Br polar covalent bonds.

It was found that more favorable reaction sites in the case of the substitution halogenation reactions permit halogen atoms to be electron-richer, which is in concordance with the widely used electronegativity scale. In principle, this result predicts an order of prospective halogenation sites using only an electrostatic charge distribution within a pristine organic cation. Efforts on further chemical modification of ionic liquids must benefit from this observation, because it fosters understanding of the resulting mixture of products and stipulates synthetic solutions to adjust its composition.

Strong cation−anion coordination is a major source of nonideal behavior in the ionic liquids. The anion was not included in this study to make results more general. It may constitute an interesting extension of the present work to investigate how different anions and solvent molecules adjust halogenation. This effect is poorly predictable, because the halogenated RTIL will exhibit a different charge density distribution and possibly different cation−anion coordination.

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Notes

The authors declare no competing financial interest.

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) Lukoshko, E.; Mutelet, F.; Domanska, U. Experimental and theoretically study of interaction between organic compounds and tricyanomethanide based ionic liquids. *J. Chem. Thermodyn.* **2015**, *85*, 49−56.

(3) Jia, C. M.; Cao, Y.; Zuo, T.; Hu, R.; Yao, T.; Song, H. Solubility of Benzothiazolium Ionic Liquids in Water and in Furfural. *J. Chem. Eng. Data* **2015**, *60*, 999−1005.

(4) Zhao, H. DNA stability in ionic liquids and deep eutectic solvents. *J. Chem. Technol. Biotechnol.* **2015**, *90*, 19−25.

(5) Fileti, E. E.; Chaban, V. V. Imidazolium Ionic Liquid Helps to Disperse Fullerenes in Water. *J. Phys. Chem. Lett.* **2014**, *5*, 1795−1800.

(6) Machanova, K.; Boisset, A.; Sedlakova, Z.; Anouti, M.; Bendova, M.; Jacquemin, J. Thermophysical Properties of Ammonium-Based Bis{(trifluoromethyl)sulfonyl}imide Ionic Liquids: Volumetric and Transport Properties. *J. Chem. Eng. Data* **2012**, *57*, 2227−2235.

(7) Muhammad, N.; Hossain, M. I.; Man, Z.; El-Harbawi, M.; Bustam, M. A.; Noaman, Y. A.; Alitheen, N. B. M.; Ng, M. K.; Hefter, G.; Yin, C. Y. Synthesis and Physical Properties of Choline Carboxylate Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2191−2196.

(8) Galonde, N.; Nott, K.; Debuigne, A.; Deleu, M.; Jerome, C.; Paquot, M.; Wathelet, J. P. Use of ionic liquids for biocatalytic synthesis of sugar derivatives. *J. Chem. Technol. Biotechnol.* **2012**, *87*, 451−471.

(9) Chaban, V. V.; Maciel, C.; Fileti, E. E. Solvent Polarity Considerations Are Unable to Describe Fullerene Solvation Behavior. *J. Phys. Chem. B* **2014**, *118*, 3378−3384.

(10) Pereiro, A. B.; Araujo, J. M. M.; Esperanca, J. M. S. S.; Marrucho, I. M.; Rebelo, L. P. N. Ionic liquids in separations of azeotropic systems - A review. *J. Chem. Thermodyn.* **2012**, *46*, 2−28.

(11) Zhao, Y.; Bostrom, T. Application of Ionic Liquids in Solar Cells and Batteries: A Review. *Curr. Org. Chem.* **2015**, *19*, 556−566.

(12) Chaban, V. V.; Maciel, C.; Fileti, E. E. Does the Like Dissolves Like Rule Hold for Fullerene and Ionic Liquids? *J. Solution Chem.* **2014**, *43*, 1019−1031.

(13) Wang, X. J.; Chi, Y. L.; Mu, T. C. A review on the transport properties of ionic liquids. *J. Mol. Liq.* **2014**, *193*, 262−266.

(14) Abro, R.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yu, G. R.; Qazi, A. B.; Gao, S. R.; Chen, X. C. A review of extractive desulfurization of fuel oils using ionic liquids. *RSC Adv.* **2014**, *4*, 35302−35317.

(15) Kalugin, O. N.; Voroshylova, I. V.; Riabchunova, A. V.; Lukinova, E. V.; Chaban, V. V. Conductometric study of binary systems based on ionic liquids and acetonitrile in a wide concentration range. *Electrochim. Acta* **2013**, *105*, 188−199.

(16) Anouti, M.; Caillon-Caravanier, M.; Le Floch, C.; Lemordant, D. Alkylammonium-based protic ionic liquids part I: Preparation and physicochemical characterization. *J. Phys. Chem. B* **2008**, *112*, 9406−9411.

(17) Belieres, J. P.; Angell, C. A. Protic ionic liquids: Preparation, characterization, and proton free energy level representation. *J. Phys. Chem. B* **2007**, *111*, 4926−4937.

(18) Yoshizawa, M.; Ohno, H. Anhydrous proton transport system based on zwitterionic liquid and HTFSI. *Chem. Commun.* **2004**, 1828−1829.

(19) Pires, J.; Timperman, L.; Jacquemin, J.; Balducci, A.; Anouti, M. Density, conductivity, viscosity, and excess properties of (pyrrolidinium nitrate-based Protic Ionic Liquid plus propylene carbonate) binary mixture. *J. Chem. Thermodyn.* **2013**, *59*, 10−19.

(20) Firaha, D. S.; Kirchner, B. CO2 Absorption in the Protic Ionic Liquid Ethylammonium Nitrate. *J. Chem. Eng. Data* **2014**, *59*, 3098−3104.

(21) MacFarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A. Energy applications of ionic liquids. *Energy Environ. Sci.* **2014**, *7*, 232−250.

(22) Yasuda, T.; Watanabe, M. Protic ionic liquids: Fuel cell applications. *MRS Bull.* **2013**, *38*, 560−566.

(23) de Vries, H.; Jeong, S.; Passerini, S. Ternary polymer electrolytes incorporating pyrrolidinium-imide ionic liquids. *RSC Adv.* **2015**, *5*, 13598−13606.

(24) Zaitsau, D. H.; Yermalayeu, A. V.; Emel'yanenko, V. N.; Heintz, A.; Verevkin, S. P.; Schick, C.; Berdzinski, S.; Strehmel, V. Structure-property relationships in ILs: Vaporization enthalpies of pyrrolidinium based ionic liquids. *J. Mol. Liq.* **2014**, *192*, 171−176.

(25) Moreno, M.; Montanino, M.; Carewska, M.; Appetecchi, G. B.; Jeremias, S.; Passerini, S. Water-soluble, triflate-based, pyrrolidinium ionic liquids. *Electrochim. Acta* **2013**, *99*, 108−116.

(26) Souckova, M.; Klomfar, J.; Patek, J. Surface tension and 0.1 MPa densities of imidazolium-, pyridinium-, pyrrolidinium-, and piperidinium-based tris(pentafluoroethyl)trifluorophosphate ionic liquids. *Fluid Phase Equilib.* **2012**, *333*, 38−46.

(27) Pejakovic, V.; Kronberger, M.; Mahrova, M.; Vilas, M.; Tojo, E.; Kalin, M. Pyrrolidinium sulfate and ammonium sulfate ionic liquids as lubricant additives for steel/steel contact lubrication. *Proc. Inst. Mech. Eng., Part J* **2012**, *226*, 923−932.

(28) Fang, S. H.; Zhang, Z. X.; Jin, Y. D.; Yang, L.; Hirano, S.; Tachibana, K.; Katayama, S. New functionalized ionic liquids based on pyrrolidinium and piperidinium cations with two ether groups as electrolytes for lithium battery. *J. Power Sources* **2011**, *196*, 5637−5644.

(29) Anouti, M.; Porion, P.; Brigouleix, C.; Galiano, H.; Lernordant, D. Transport properties in two pyrrolidinium-based protic ionic liquids as determined by conductivity, viscosity and NMR self-diffusion measurements. *Fluid Phase Equilib.* **2010**, *299*, 229−237.

(30) Appetecchi, G. B.; Kim, G. T.; Montanina, M.; Carewska, M.; Marcilla, R.; Mecerreyes, D.; De Meatza, I. Ternary polymer electrolytes containing pyrrolidinium-based polymeric ionic liquids for lithium batteries. *J. Power Sources* **2010**, *195*, 3668−3675.

(31) Cui, Y. G.; Biondi, I.; Chaubey, M.; Yang, X.; Fei, Z. F.; Scopelliti, R.; Hartinger, C. G.; Li, Y. D.; Chiappe, C.; Dyson, P. J. Nitrile-functionalized pyrrolidinium ionic liquids as solvents for cross-coupling reactions involving in situ generated nanoparticle catalyst reservoirs. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1834−1841.

(32) Emel'yanenko, V. N.; Verevkin, S. P.; Heintz, A.; Corfield, J. A.; Deyko, A.; Lovelock, K. R. J.; Licence, P.; Jones, R. G. Pyrrolidinium-based ionic liquids. 1-butyl-1-methyl pyrrolidinium dicyanoamide: Thermochemical measurement, mass spectrometry, and ab initio calculations. *J. Phys. Chem. B* **2008**, *112*, 11734−11742.

(33) Voroshylova, I. V.; Chaban, V. V. Atomistic Force Field for Pyridinium-Based Ionic Liquids: Reliable Transport Properties. *J. Phys. Chem. B* **2014**, *118*, 10716−10724.

(34) Chaban, V. V.; Prezhdo, O. V. Polarization versus Temperature in Pyridinium Ionic Liquids. *J. Phys. Chem. B* **2014**, *118*, 13940−13945.

(35) Chaban, V. V.; Prezhdo, O. V. Water Phase Diagram Is Significantly Altered by Imidazolium Ionic Liquid. *J. Phys. Chem. Lett.* **2014**, *5*, 1623−1627.

(36) Tan, K. L.; Li, C. X.; Meng, H.; Wang, Z. H. Improvement of Hydrophobicity of Ionic Liquids by Partial Chlorination and Fluorination of the Cation. *Chin. J. Chem.* **2009**, *27*, 174−178.

(37) Nanse, G.; Papirer, E.; Fioux, P.; Moguet, F.; Tressaud, A. Fluorination of carbon blacks: An X-ray photoelectron spectroscopy study 0.1. A literature review of XPS studies of fluorinated carbons. XPS investigation of some reference compounds. *Carbon* **1997**, *35*, 175−194.

(38) Hollitzer, E.; Sartori, P. Electrochemical Fluorination - a Review. *Chem. Ing. Tech.* **1986**, *58*, 31−38.

(39) Cizek, J. Origins of Coupled Cluster Technique for Atoms and Molecules. *Theor Chim Acta* **1991**, *80*, 91−94.

(40) 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.

(41) Wales, D. J.; Scheraga, H. A. Review: Chemistry - Global optimization of clusters, crystals, and biomolecules. *Science* **1999**, *285*, 1368−1372.

(42) Dupradeau, F. Y.; Pigache, A.; Zaffran, T.; Savineau, C.; Lelong, R.; Grivel, N.; Lelong, D.; Rosanski, W.; Cieplak, P. The R.ED. tools: advances in RESP and ESP charge derivation and force field library building. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7821−7839.

(43) 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.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. General Atomic and Molecular Electronic-Structure System. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(44) Teixeira, F.; D. S. Cordeiro, M. N. Simple descriptors for assessing the outcome of aza-Diels-Alder reactions. *RSC Adv.* **2015**, *5*, 50729−50740.