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Structure-property relationships in ionic liquids: Chain length dependence of the vaporization enthalpies of imidazolium-based ionic liquids with fluorinated substituents

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ABSTRACT

Molar vaporization enthalpies of fluoroalkyl-substituted imidazolium-based ionic liquids were derived from two concurring quartz crystal microbalance (QCM) and thermogravimetry (TGA) methods. For comparison, enthalpies of vaporization measured at elevated temperatures have been adjusted to the reference temperature 298 K and tested for consistency. It was found that vaporization enthalpies of fluorine substituted families are significantly higher compared to the analogous ILs with the alkyl-substituted cation. This is in agreement to molecular solvents, where fluorination typically increases vaporization enthalpy relative to hydrocarbon analogues. A useful group contribution for the incremental CF_2 fragment in the alkyl chain was recommended for the quick estimation of vaporization enthalpies of various substituted IL cations (e.g., imidazolium, ammonium, pyridinium, etc.).

1. Introduction

The large bond energy of carbon-fluorine bonds imparts excellent chemical and thermal stability to organofluorine compounds [1]. Furthermore, fluorinated compounds are typically both hydrophobic and lipophobic which creates unique interfacial and solution behaviors, which has been attributed to the low polarizability of fluorine atoms and the weak dispersion forces that occur between polyfluorinated molecules. Yet fluorinated solvents also tend to exhibit increased capacity relative to hydrocarbons for absorbing gases such as O_2, with perfluorodecalin having been employed as a "blood substitute". Because of the unique physical and chemical properties associated with organofluorine compounds, these substances find use in a variety of applications such as refrigerants, polymers, lubricants and surfactants.

In terms of the vast majority of ionic liquid (IL) research publications, the inclusion of fluorine atoms has occurred within the anion rather than the cation. A number of inorganic and organic anionic species containing fluorine have been employed in IL synthesis, including: tetrafluoroborate [BF_4], hexafluorophosphate [PF_6], triflate [OTf], bistriflimide [NTf_2] and tris(perfluoroalkyl)trifluorophosphate (FAP) [2]. Typically, these anions are paired with a cationic species that is functionalized with alkyl substituents, such as 1-butyl-3-methylimidazolium ([C_4mim]). Interestingly, studies of the absorption of poly- and perhalogenated refrigerants (e.g., R-11, R-113, R-123 and R-134a) by ILs have focused on such IL systems as [C_4mim][PF_6] and [C_6mim][NTf_2] where the fluorine atoms were solely contained in the anion [3–8]. These studies demonstrated that perhaloganted compounds were much less soluble in the ILs with fluorinated anions compared to polyhalogenated compounds that contain an H atom. This behavior is attributed to H-bonding between the halogenated compound and the IL.

Increasing the fluorine content of the IL through cation functionalization for absorption applications would seem to be an interesting avenue to pursue, but such studies have not yet been performed. Imidazolium-based ILs bearing fluoroalkyl substituents appended to the cation appear to be exceedingly rare in the literature. One reason may be the much greater expense of the requisite fluoroalkyl precursors (e.g., 1,1,1,2,2-pentafluoro-4-iodobutane) in comparison to analogous alkyl halides (e.g., 1-bromobutane) and/or a larger number of chemical transformations required to produce the final product [9].

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The limited data on fluoroalkyl-containing imidazolium-based ILs available in the literature are primarily focused on species with the general structure shown in Fig. 1, herein denoted as $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ where n is equal to the number of fluorinated carbons in the side chain and the total number of fluorine atoms present in the side chain is $2n+1$.

To date, studies on these $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs have been focused on physical property characterization [10,11], CO_2 solubility/separation [10,12,13] and molecular dynamics (MD) simulations [11,14]. A recent review of the state of MD simulations, including efforts focused on ILs has been published by Palmer and Debenedetti [15]. Experimental and computational results revealed that $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs were significantly denser and more viscous than their $[C_nmim][Tf_2N]$ analogues containing the same number of carbon atoms. Furthermore, Bara et al. also observed that $[C_8F_{17}C_2H_4mim][NTf_2]$ was crystalline at ambient temperature ($T_m \sim 30\,^\circ C$) while $[C_{10}mim][NTf_2]$ remains liquid well-below this temperature [10]. With the exception of density, increased viscosity and melting point are not typically associated with fluorocarbons relative to their analogous hydrocarbons.

CO_2 absorption and separation properties were observed to improve in $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs, but did not yield dramatic improvements. Horne et al. [15] recently proposed that $[C_nF_{2n+1}CH_2mim][NTf_2]$ ILs actually possess smaller amounts of accessible space for gases to dissolve, an effect which may offset any enhanced affinity that CO_2 or O_2 may have for the fluoroalkyl functionalities [16].

Molecular dynamics [15] simulations have confirmed experimental observations and illustrated the structuring of the $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs is distinctly different than the aggregates observed in alkyl- or ether-functionalized cations with similar side chain length. MD simulations illustrated that for $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs, the electron-withdrawing character of fluorine causes the CH_2 group attached to the N(1) position of the imidazolium ring to possess a larger partial positive charge than in $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs. The anion is able to interact more strongly with, and more closely approach the cation due to the larger region(s) of partial positive charge surrounding the imidazolium ring. These additional interactions cause decreased dynamics (i.e., increased viscosity) and may also account for the increased melting point previously observed. The enhanced structuring/aggregation tendencies of $[C_nF_{2n+1}C_2H_4mim]$ cations has more recently been used to synthesize ionic liquid crystals with lamellar and smectic A (SmA) mesophases [17].

MD simulations of $[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs have also predicted increased enthalpies of vaporization on the order of 5 kJ mol^{-1} relative to analogous $[C_nmim][NTf_2]$ ILs. Here, we report experimental results on the vaporization of a series of four fluoroalkyl-functionalized ILs (cf. Fig. 1). Similar to results obtained in our prior works [18–21] and those of others in this area, a linear relationship between IL cation chain length and vaporization enthalpy has been observed. The results indicate that the presence of fluoroalkyl chains increases the enthalpy of vaporization of ILs when compared to alkyl or oligo(ethylene glycol) groups. ^{1}H NMR experimental data and COSMOTherm simulations provide further evidence that increased cation–anion interactions are present due to the electron-withdrawing character of the fluorine atoms, and may contribute to the increase vaporization enthalpy. A group contribution increment for the CF_2 linkage to aid in rapid estimation of vaporization enthalpies is also reported.

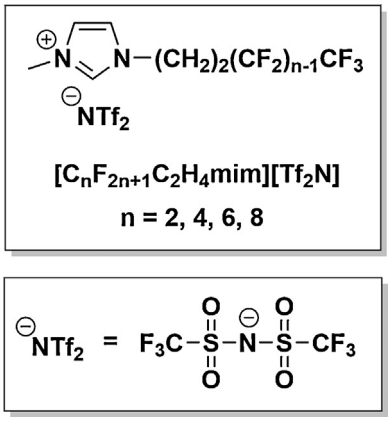

Fig. 1. General structure of fluoroalkyl-functionalized imidazolium-based ILs (top) and structure of $[NTf_2]$ anion (bottom).

2. Materials and methods

2.1. Materials

$[C_nF_{2n+1}C_2H_4mim][NTf_2]$ ILs were synthesized according to procedures previously published by Bara et al. [10]. ^{1}H and ^{19}F NMR data were consistent with our previously published results [10]. Prior to the vaporization experiments, the ILs were dried by vacuum evaporation at 333 K and 10^{-3} mbar for at least 24 h. IL samples were subjected to additional purification inside of the experimental equipment in order to remove possible traces of volatile impurities.

2.2. Measurements of vaporization enthalpies by the quartz crystalline microbalance (QCM)

Molar enthalpies of vaporization of ILs were measured using the QCM method. The vaporization enthalpies were derived from the temperature dependences of the experimentally measured change in the vibrational frequency of the quartz crystal. The experimental setup was developed for measuring of compounds with the extremely low vapor pressures, and we have recently reported on the use of this approach with ILs [18,22]. This technique is principally different from the well-established Knudsen-technique. In contrast to the Knudsen method, where the sample cell is closed with a membrane and only a small hole connects the sample container to the vacuum, in our method a sample of an IL is placed in an open cavity (Langmuir evaporation) inside of the thermostatted block and it is exposed to vacuum (10^{-5} Pa) with the whole open surface of the loaded compound. The QCM is placed directly over the measuring cavity containing the sample. During the vaporization into vacuum, a certain amount of sample is deposited on the quartz crystal. The change of the vibrational frequency Δf was directly related to the mass deposition Δm on the crystal according to equation:

$$\Delta f = C \times f^2 \times \Delta m \times S_C^{-1} \quad (1)$$

where f is the fundamental frequency of the crystal (6 MHz in this case) with $\Delta f \ll f$, S_C is the surface of the crystal, and C is a constant [23]. Using the frequency change rate df/dt measured by the QCM the molar enthalpy of vaporization, $\Delta_l^g H_m^\circ(T_0)$, is obtained by:

$$\ln\left(\frac{df}{dt}\sqrt{T}\right) = A' - \frac{\Delta_l^g H_m^\circ(T_0) - \Delta_l^g C_{p,m}^\circ T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_l^g C_{p,m}^\circ}{R}\ln\left(\frac{T}{T_0}\right) \quad (2)$$

where the constant A' is essentially unknown and includes all empirical parameters specific to the apparatus and the substance under study. T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature, which we have set to 298.15 K. The value

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