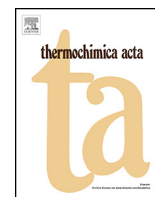




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Structure–property relationships in ionic liquids: Chain length dependence of the vaporization enthalpies of imidazolium-based ionic liquids with fluorinated substituents



Dzmitry H. Zaitsau^{a,*}, Andrei V. Yermalayev^b, Sergey P. Verevkin^{a,b}, Jason E. Bara^{c,**}, David A. Wallace^c

^a Department of Physical Chemistry, Kazan Federal University, 420008 Kazan, Russia

^b Department of Physical Chemistry and Department, Science and Technology of Life, Light and Matter, University of Rostock, D-18059, Rostock, Germany

^c University of Alabama, Department of Chemical & Biological Engineering, Tuscaloosa, AL 35487-0203, USA

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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 CF₂ 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.).

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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 O₂, 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 [BF₄], hexafluorophosphate [PF₆], triflate [OTf], bistriflimide [NTf₂] 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 ([C₄mim]). 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 [C₄mim][PF₆] and [C₆mim][NTf₂] where the fluorine atoms were solely contained in the anion [3–8]. These studies demonstrated that perhalogenated 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].

* Corresponding author. Tel.: +49 381 498 6508; fax: +49 381 498 6524.

** Corresponding author. Tel.: +1 205 348 6836; fax: +1 205 348 7558.

E-mail addresses: zaitsaudz@gmail.com, dzmitry.zaitsau@uni-rostock.de (D.H. Zaitsau), jbara@eng.ua.edu (J.E. Bara).