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# The ability of ionic liquids to form hydrogen bonds with organic solutes evaluated by different experimental techniques. Part I. Alkyl substituted imidazolium and sulfonium based ionic liquids

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## ABSTRACT

This work is devoted to the quantitative study of hydrogen bond formation of *N*-alkyl substituted ionic liquids with proton acceptor and proton donor organic solvents. 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide [BMIM][NTf<sub>2</sub>], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][TfO], 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>], triethylsulfonium bis(trifluoromethylsulfonyl)imide [Et<sub>3</sub>S][NTf<sub>2</sub>], 1-butyl-3-methylimidazolium tricyanomethanide [BMIM][TCM], 1-hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF<sub>4</sub>] were investigated by solution calorimetry and FTIR-spectroscopy techniques. The stretching vibration region of C=O group of 2-pentanone in mixture with *N*-alkyl substituted ionic liquid in inert solvent carbon tetrachloride was analyzed at different concentrations of components for the estimation of proton donor ability of ionic liquids. Also, the stretching vibration region of the OH-group of methanol was studied in a ternary system carbon tetrachloride (inert solvent), methanol (proton donor) and *N*-alkyl substituted ionic liquid for the estimation of proton acceptor ability of ionic liquids. The hydrogen bond enthalpy of methanol in ionic liquids was calculated using data of measured solution enthalpies and data extracted from the literature. The frequency shifts of the OH-group of methanol induced by intermolecular interactions within ionic liquids in a carbon tetrachloride solution were compared with the hydrogen bonding enthalpies of methanol with ionic liquids. A linear relationship between the frequency shifts of the OH-groups and hydrogen binding enthalpies of methanol in ionic liquids were found. According to measured FTIR-spectroscopy data, the *N*-alkyl substituted ionic liquids analyzed in this work possess weak proton donor properties, and at the same time their proton acceptor ability (basicity) is much higher and shows dependency on anion structure.

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## 1. Introduction

One of the most important tasks of modern chemistry is related to the design of new materials; one such example of interest is the use of ionic liquids. This class of molten salts usually consists of bulky organic cations and organic/inorganic anions. Some of the ionic liquids properties including, negligible vapor pressure and wide temperature ranges in the liquid state, offer a new perspective for industrial applications and settings. In this regard, ionic liquids can be used as media for organic synthesis reactions, as solvents for poorly soluble compounds and as chemical agents in separation processes [1–3]. Efficiency of all these applications depends on the strength of intermolecular interactions of dissolved molecules within ionic liquids. Therefore, methods for evaluating the intermolecular interactions of organic compounds in ionic liquids

play a key role in the full-scale application of ionic liquids in the chemical industry.

There are two thermodynamic approaches for quantification of intermolecular interactions of organic molecules in ionic liquids. The first approach is based on using the multi-parameter correlations for description of thermodynamic functions of solution or solvation. This approach can be applied for two types of solute-solvent systems: (1) one solute dissolves in a series of solvents [4] (Kamlet-Taft-Abbod); (2) a series of solutes dissolves in one solvent [5] (Abraham). Two types of multiparameter correlation were applied previously to study intermolecular interactions and solvation properties of various solute-ionic liquid systems [6–9].

The second approach is based on the separation of thermodynamic functions of solvation on contributions of non-specific solvation (van der Waals interactions) and specific solvation (hydrogen bonding, donor-acceptor interactions). This approach was applied for studies of ionic liquids solutions [10–14]. It was observed that the dipole moment of solute molecules do not affect the solvation enthalpy in ionic liquids [10]. Recently, the group contribution approach was successfully

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