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# Enthalpies of solution of 1-ethyl- and 1-butyl-3-methylimidazolium based ionic liquids in tetrahydrofuran and chloroform at 298.15 K: Thermochemical proton acceptor scale of anions



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## ABSTRACT

In this work the thermodynamics of intermolecular interactions for imidazolium based ionic liquids in solutions of proton donor solvent chloroform and proton acceptor solvent tetrahydrofuran was studied using solution calorimetry technique. Enthalpies of solution of 1-ethyl- and 1-butyl-3-methylimidazolium based ionic liquids with tetrafluoroborate, methylsulfate, ethylsulfate, butylsulfate, dicyanoamide, trifluoromethanesulfonate, thiocyanate anions were measured in two solvents over concentration range 0.18–3.60 mmol kg<sup>-1</sup> at 298.15 K. Enthalpies of transfer from tetrahydrofuran to chloroform derived from experimental data were exothermic for all studied ionic liquids. Proton acceptor scale of ionic liquids as solutes was proposed on the basis of thermochemical data. Enthalpy of hydrogen bonding of ionic liquids with proton donor solvent chloroform increases in the range of anions [BF<sub>4</sub>]<sup>-</sup> < [SCN]<sup>-</sup> < [TfO]<sup>-</sup> < [N(CN)<sub>2</sub>]<sup>-</sup> < [AlkSO<sub>4</sub>]<sup>-</sup>. At the same time these values remain constant for ILs with different length of alkyl group in cations and anions. Thermochemical proton acceptor scale of ILs in solution correlates well with COSMO-RS hydrogen-bonding energies in equimolar cation–anion pairs of ILs.

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## 1. Introduction

Nowadays, the rapidly growing interest in a perspective class of molten salts known as ionic liquids (ILs) is observed. The reason of this interest lies in a variety of possible applications of ionic liquids due to their unique properties which include high thermal stability, wide liquid state temperature range, good solvation ability, negligible vapor pressure, non-flammability and high conductivity. Therefore, ILs can be used in different areas of chemical industry such as “green” solvents, homogeneous and biphasic transfer catalysts, and *etc.* [1]. Also, according to experimental results [2] they are attractive candidates in separation processes and extraction in the liquid–liquid systems. Another perspective area of practical application of ILs is using them as effective co-solvents in the different physical–chemical processes. Buchfink et al. [2] have shown that imidazolium based ionic liquids act as suppressors of protein aggregation and effectively promote the *in vitro* refolding of denatured proteins in aqueous solution. Their performance as refolding

enhancers significantly depends on the anion of ionic liquids. In work [3] ILs as co-solvents have shown a great potential to enhance enzymatic hydrolysis of rutin for isoquercitrin production. Also, mixtures of ionic liquids with organic solvents were identified as more preferable solvents for homogeneous derivatization of cellulose than pure components [4–6]. Efficiency of cellulose dissolution is changed depending the structure of organic solvent and ionic liquid.

Prediction of physical–chemical behavior of ILs based co-solvent systems requires data on solubility of ionic liquids in organic media and knowledge of strength of intermolecular interactions in these binary mixtures. Solution calorimetry is a suitable technique for determination of these data. The enthalpies of solution of ionic liquids in organic solvents represent the temperature coefficients of solubility data. Also, these values can be used as original sources for quantification of intermolecular interactions in solution. However, in literature only limited data on the enthalpies of solution of ILs in organic media are available. The general part of experimental studies was devoted to the dissolution of ILs in water [8–13]. Brennecke et al. [7] were one of the first who determined enthalpies of solution at infinite dilution of imidazolium based ILs with different anions in aqueous media by UV–vis spectroscopy. Coutinho and co-workers [8,9] have analyzed effect of alkyl chain length on the

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