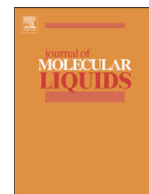




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Group additivity approach for determination of solvation enthalpies of aromatic compounds in 1-butyl-3-methylimidazolium tetrafluoroborate based on solution calorimetry data



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ABSTRACT

In this work thermochemistry of solvation of mono-, di-, tri- and tetra-substituted benzenes in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) ionic liquid was studied. Enthalpies of solution at infinite dilution of 34 substituted benzenes in [BMIM][BF₄] were measured at 298.15 K using solution calorimetry technique. Based on the experimental and literature data enthalpies of solvation of 36 substituted benzenes in [BMIM][BF₄] were calculated. It was shown that enthalpies of solvation of substituted benzenes in [BMIM][BF₄] are independent on the mutual position of substituents and dipole moment of molecules. Group contribution scheme for prediction of enthalpies of solvation of substituted benzenes was applied. Values of methyl- (CH₃), *tert*-butyl- (*tert*-C₄H₉), bromo- (Br), iodo- (I), amino- (NH₂), methoxy- (OCH₃), dimethylamino- (N(CH₃)₂), methylcarboxylate- (COOCH₃) group contributions to the enthalpies of solvation in [BMIM][BF₄] were derived and compared with molecular solvents. Solvation enthalpies of substituted benzenes in [BMIM][BF₄] calculated through group contribution scheme were in good agreement with experimental data.

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1. Introduction

Ionic liquids present a perspective type of organic salts which cause a growing interest among researchers. Typically ionic liquids consist of bulky organic cation and inorganic or organic anion. The most interesting of them are room temperature imidazolium-based and further in the text ionic liquids (RTIL). These organic salts have negligible vapor pressure, high solvency ability, wide temperature range of liquid state and very low flammability. As a result, they can be applied in industry as a universal media for synthesis, extraction, dissolution and separation processes [1–4]. Studies of the thermochemistry of solvation of organic compounds in imidazolium based ionic liquids are very important for their practical application. First, enthalpies of solvation can give quantitative information about temperature effect on solubility data in imidazolium based ionic liquids. Second, the enthalpies of solvation present the overall measure of solute-solvent intermolecular interactions, which governs dissolution processes. Experimental determination of solvation enthalpies is time and substance consuming procedure, especially for ionic liquids due to high cost and difficulties of purification. So, empirical methods for fast prediction of solvation enthalpy values in ionic liquids are required. These empirical methods can be based on different multi-parameter correlations and group

contribution schemes. The most widely used of them was LSER approach developed by Acree and Abraham [5]. This approach is based on multi-parameter correlations of solvation enthalpies and six solute descriptors: hydrogen-bond acidity (A) and basicity (B), excess molar refraction (E), dipolarity/polarizability (S), McGowan volume (V) and gas-to-hexadecane partition coefficient (L), respectively. Acree and Abraham have shown applicability of LSER approach for prediction enthalpies of solvation of organic compounds in aprotic ionic liquids [6–8]. Further, LSER approach was modified and used by various groups of authors not only for determination of solvation enthalpies [9–12], but also for gas-to-ionic liquid and solvent-to-ionic liquid partition coefficients [13–21]. For application of LSER approach for determination of solvation enthalpy of any organic compound in certain ionic liquid we need to know all descriptors for studied solute. Also, solvation enthalpies of various classes of organic compounds in this ionic liquid are required for correct evaluation of regression coefficients of multi-parameter correlation.

Another alternative method for prediction of solvation enthalpies in ionic liquids is based on group additivity approach. This approach was proposed and successfully used for molecular solvents [22]. Recently, it was shown that group contribution approach can be applied for solutions of chloro- and nitro-substituted benzenes in three ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [23].

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