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The hydrogen bonding enthalpies of water and methanol in ionic liquids

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ABSTRACT

The thermochemical study of hydrogen bonding of water with different proton acceptor ionic liquids was carried out. Along with the available experimental data, the solution enthalpies of water in [BMIM][TfO], [BMIM][BF_4] and [BMIM][PF_6] were measured. The hydrogen bonding enthalpies of water with various ionic liquids were determined by using previously developed method of solvation enthalpy separation into the nonspecific solvation enthalpy and the specific solute-solvent interaction enthalpy (hydrogen bonding). The findings indicate the formation of a complex, where one molecule of water is bound to two molecules of ionic liquids. Similarly, hydrogen bonding enthalpies of methanol with the same proton acceptor ionic liquids were determined.

1. Introduction

Ionic liquids (IL) have a some unique properties: negligibly low vapor pressure, wide temperature range of the liquid state. Due to these properties IL are widely used as solvents in various fields of science and industry [1–4]. Purposeful use of IL requires knowledge of quantitative parameters of intermolecular interactions (in particular, the hydrogen bonding enthalpies) solute-ionic liquid. In a series, works [5–9], the solvating ability of ILs is described by multiparameter equations. In work [10] the effect of the solute's dipole moment on the solvation enthalpy was investigated. Contrary to common expectations, the solvation enthalpies of the studied compounds in IL are almost independent on solute’s dipole moment.

Although, solute-solvent hydrogen bonding energy can have an insignificant contribution to the thermodynamic functions of solvation, it has a decisive influence on the reactivity of solute in the solvent. In the work [11], hydrogen bonding enthalpies of proton donor organic nonelectrolytes (aliphatic alcohols, diols, anilines, chloroform formamide) with different proton acceptor IL were determined. It was shown that the hydrogen bonding enthalpy of proton donor solutes with IL increases in the anion series: tetrafluoroborate ≈ bis(trifluoromethylsulfonyl)imide < 2-(2-methoxyethoxy)ethyl sulfate < trifluoromethanesulfonate.

In the work of the Ludwig et al [12] it was shown by IR-spectroscopy, that the water molecule forms a hydrogen bond with the IL either in the form of a hydrogen-bound 1:1 complex or in a 1:2 complex. However, data on hydrogen bonding enthalpies of water molecule with proton acceptors ionic liquids are limited [13]. Common methods for determining the hydrogen bonding enthalpy (IR spectroscopy) are hardly applicable for such systems. For direct determination of hydrogen bond enthalpies of a water molecule in IL using IR-spectroscopy an exact concentration of monomeric water and ionic liquid in an inert solvent medium must be prepared [14]. This is often impossible since the molecules of ILs and water in such conditions are self-associated In [13] authors have obtained hydrogen bond enthalpies of water in ionic liquids using ATR-IR spectroscopy. The hydrogen bond enthalpies of water in ionic liquids were estimated from spectral shifts. It should be noted, that for the estimation of hydrogen bond enthalpies of water in ionic liquids an empiric equation was used. This equation has significant uncertainty in the values of the variables [15].

In work [16] the hydrogen bonding enthalpies of water molecule with various proton acceptors compounds (*N,N*-dimethylformamide, acetonitrile, tetrahydrofuran, 1,4-dioxane, acetone, dimethylsulfoxide, *N,N*-dimetylacetamide) were determined using solution calorimetry method. It was shown that hydrogen bond enthalpy of water with proton acceptors is approximately twice the hydrogen bond enthalpy of methanol with the same proton acceptors. In present work the hydrogen bond enthalpies of water in ionic liquids were determined based on solution calorimetry data. The hydrogen bonding enthalpies of methanol and water in molecular solvents and ILs were compared. This reveals particular features of solute-solvent hydrogen bonds in ionic liquids in comparison with molecular solvents.

2. Experimental part

2.1. Materials

The [BMIM][BF_4], [BMIM][TfO], [BMIM][PF_6], were supplied by

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