Hydrogen bonding of molecular solutes in protic and aprotic ionic liquids

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ABSTRACT

The thermochemical study of hydrogen bonding of organic solutes in 1-methylimidazolium bis(trifluoromethylsulfonyl)imide ([MIM][NTf$_2$]) was carried out. Activity coefficients at infinite dilution of organic compounds in [MIM][NTf$_2$] were measured by gas-liquid chromatography at different temperatures between 303.15 and 343.15 K. The solution enthalpies of organic solutes in [MIM][NTf$_2$] were determined from the temperature dependence of activity coefficients in the same systems. Solution enthalpies of solutes (propanol-1, meta-cresol, acetone, acetonitrile, diethyl ether, tetrahydrofuran, dichloromethane, trichloromethane, pyrrole) in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTf$_2$] were measured by using high-precision solution calorimetry. The hydrogen bond enthalpies of organic solutes in [MIM][NTf$_2$] and [BMIM][NTf$_2$] were calculated using a previously developed method. The hydrogen bond enthalpies of organic solutes in the protic ionic liquid [MIM][NTf$_2$] were compared with the values in the aprotic ionic liquid [BMIM][NTf$_2$], as well as with those in the molecular solvent pyrrole. The hydrogen bond enthalpies of proton acceptor molecules in [MIM][NTf$_2$] differ significantly from zero unlike in [BMIM][NTf$_2$]. Hydrogen bond enthalpies of proton acceptor molecules in [MIM][NTf$_2$] and pyrrole are close.

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1. Introduction

A new class of molten salts known as ionic liquids (ILs) is among the promising novel materials for the chemical industry. The interest in ionic liquids is due to their properties: negligible vapor pressure and wide temperature range in the liquid state. However, mostly the aprotic ILs (AILs) have been in the focus of contemporary studies. Only recently, thermodynamic studies with few protic ionic liquids (PILs) have been performed [1–5]. PILs can be used as electrolytes for batteries [6,7], as biosensors [8], as anticancer agents [9,10]. The quantitative evaluation of intermolecular interactions in organic solute/PIL systems is a key factor in allowing the application of protic ionic liquids to different tasks. However, intermolecular interactions of dissolved molecules in PILs not have been studied in detail. Moreover, an important question "how much different intermolecular interactions in PILs, compared to AILs" should be elucidated.

Activity coefficients at infinite dilution, $\gamma_{1,3}^{\infty}$, provide significant amount of thermodynamic information required for an assessment of intermolecular interactions of organic molecular solutes in ionic liquids. For example, activity coefficients $\gamma_{1,3}^{\infty}$ of 54 solutes at different temperatures in PILs with common cation containing acidic hydrogen were measured [11]. It was demonstrated that the separation/extraction

selectivity of PIL was lower than those of conventional solvents and AILs. Shukla et al. [12] studied the polarity of PILs containing protic anion by using the multi-parameter equation (Kamlet-Taft-Abboud). It was shown that the acidic and basic properties of PILs are stronger than that of AILs.

The new tool for the analysis of intermolecular interactions of solutes in the solvent was proposed previously in [13]. This approach permits evaluation of the various contributions of intermolecular interactions to the thermochemical solvation parameters. This approach was successfully applied in the recent past [14] to the solute/AILs systems. Also, it was shown that the contribution of a dipole moment of the solute molecule into the solvation enthalpy in three ionic liquids is negligible [15]. Moreover, it has been demonstrated that solvation enthalpies of aromatic solutes in 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$] can be calculated using an additive scheme [16]. In [14] the equation for the quantification of hydrogen bonding enthalpies of organic non-electrolytes in AILs was proposed. It was shown that hydrogen bond enthalpies of proton acceptor molecules in AILs are close to zero. On the contrary, the hydrogen bond enthalpies of proton donor molecules in the same AILs are different and strongly anion dependent [14].

In this paper, the hydrogen bond enthalpies of proton donor and proton acceptor compounds in the protic ionic liquid 1-methylimidazolium bis(trifluoromethanesulfonyl)imide [MIM][NTf$_2$] were derived with the help of experimental activity coefficients $\gamma_{1,3}^{\infty}$.

A data set of different solutes (proton donors and proton acceptors) have been selected for comparison of hydrogen bond enthalpies in protic ionic liquid [MIM][NTf$_2$] and aprotic ionic liquid 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [BMIM][NTf$_2$]. Moreover, the comparison of hydrogen bond enthalpies of proton acceptors was extended for a molecular solvent (pyrrole C$_4$H$_5$N, in this study). Such a comparisons is important for understanding of changes in acidic properties of the cation of ionic liquids relative to the molecular solvent.

2. Experimental part

2.1. Materials

Ionic liquids [MIM][NTf$_2$] and [BMIM][NTf$_2$] were supplied by Sigma Aldrich and Iolitec with mass fractions higher than 0.98. Before measurements, ILs were purified from traces of volatile impurities and water by vacuum evaporation at low pressure 5×10^{-2} Pa and $T = 338$ K. The organic solutes were supplied by Sigma Aldrich with mass fraction purities higher than 0.99. Before all experiments, solutes were purified by standard techniques [17]. The purity of organic solute samples was analyzed using gas chromatography (Agilent 7890 B gas chromatograph). The water content in the ionic liquids and organic solutes was determined by a Karl Fischer titration method using an automatic titrator C20 (Mettler Toledo). Detailed information about the samples studied in this work can be found in Table S1.

2.2. Gas chromatography: Activity coefficients at infinite dilution of organic solutes in [MIM][NTf$_2$]

The ionic liquid (solvent) was used as a stationary phase covering solid support in a short packed column. Different volatile organic solutes were injected in the GC column. Their retention times were measured, and activity coefficients at infinite dilution $\gamma_{1,3}^{\infty}$ as well as partial molar excess enthalpy at infinite dilution, $\Delta_{soln}H^{A/IL}$, were derived according to the well-established procedure [18]. Solid support (Chromosorb W/AW-DMCS 100/120 mesh) coated with the ionic liquid was obtained by dispersing a certain amount of the chromosorb in the solution of the ionic liquid in dichloromethane followed by slow evaporation of the solvent. The amount of [MIM][NTf$_2$] on the solid support was 1.223×10^{-3} mol. The experimental measurements were performed with a Hewlett-Packard gas chromatograph equipped with a flame-ionization detector. Nitrogen was used as a carrier gas. Small portions of solutes (0.5 to 2) μL were injected into the GC column, and retention times were recorded by an integrator. The methane retention time was used for determination of the dead time at each experimental temperature. The retention times were reproducible within 0.01–0.03 min. The experiments were carried out at five temperatures (in five steps) between 303.15 and 343.15 K. The temperature of the GC column was constant within ±0.1 K. The detailed description of the GC measurement procedures was published elsewhere [18] and additional information is also given in the Supporting Information Table S2. The thermal stability of [MIM][NTf$_2$] inside the GC column was systematically checked by measuring the retention time of *n*-decane at 298.15 K.

2.3. Solution calorimetry

The solution enthalpies were measured at $T = 298.15 \pm 0.01$ K using TAM III TA Instruments precision isothermal solution calorimeter. The solution enthalpy of propan-1-ol in water was used as a standard for calorimetric measurements. The value obtained in this study (-10.16 ± 0.03 kJ mol^{-1}) coincides with the recommended literature data [19]. A detailed description of experimental technique and measurement procedure was published previously [20] and is also present in the supporting material. Titration technique was used for the dissolution

of the organic molecules in the ionic liquids: portions of solute (10 μL) were dropped automatically into an ionic liquid using the electronically operated microliter syringe. The syringe is equipped with a long gold cannula immersed in the calorimetric cell with solvent (ionic liquid). Experimental measurements with each solute were repeated at least six times. All measured solution enthalpies are presented in Supporting material Table S3.

3. Result and discussion

Activity coefficients of infinitely diluted organic solutes in [MIM][NTf$_2$] were measured in the present work. Temperature dependences of $\gamma_{1,3}^{\infty}$ values for each solute were approximated by the linear regression,

$$\ln \gamma_i^{\infty} = a + \frac{b}{T} \tag{1}$$

Temperature ranges, coefficients a and b, as well as the values of $\gamma_{1,3}^{\infty}$ at 298.15 K calculated by Eq. (1) are listed in Table 1. Primary data on $\gamma_{1,3}^{\infty}$ at each temperature is available in the Supporting information in Table S2. Correlation of $\ln \gamma_i^{\infty}$ values with the number of carbon atoms for different classes of solutes in [MIM][NTf$_2$] at 298.15 K are presented in Fig. 1. The activity coefficients of linear *n*-alkanes and aliphatic alcohols increase with increasing the chain length. Such a behavior serves as an evidence of the data consistency.

The values of the partial molar excess enthalpy at infinite dilution $\Delta_{soln}H^{A/IL}$ can be derived from the slope of a straight line derived according to the following equation:

$$\left(\frac{\partial \ln \gamma_i^{\infty}}{\partial (1/T)} \right) = \frac{\Delta_{soln}H^{A/IL}}{R} \tag{2}$$

where R is the universal gas constant. The $\Delta_{soln}H^{A/IL}$ values of the studied compounds are also collected in Table 1. The uncertainties of $\Delta_{soln}H^{A/IL}$ are estimated to be not higher than ±10% due to the small slope of $\ln \gamma_i^{\infty}$ versus $1/T$ plots and taking the experimental uncertainty of the γ_i^{∞} values into account.

The solution enthalpies of solutes (propanol-1, *meta*-cresol, acetone, acetonitrile, diethyl ether, tetrahydrofuran, dichloromethane, trichloromethane and pyrrole) in [BMIM][NTf$_2$] were measured by using high-precision solution calorimetry. Available literature data on

Table 1
Experimental results of γ_i^{∞} for different solutes in the [MIM][NTf$_2$]: temperature ranges, coefficients of Eq. (1), γ_i^{∞} at 298.15 K, and $\Delta_{soln}H^{A/IL}$ values derived from Eq. (2).

Solute i	Temperature range/K	a[a]	b/K[a]	γ_i^{∞}[a] (298.15 K)	$\Delta_{soln}H^{A/IL}$ /kJ·mol^{-1}
n-Octane	303–333	−0.15	1457	114	12.1
n-Nonane	303–343	−0.64	1757	191	14.6
n-Decane	303–343	−0.84	1983	333	16.5
n-Undecane	303–343	−1.48	2340	580	19.5
n-Dodecane	303–343	−1.81	2529	788	21.0
Methanol	313–343	−1.93	507	0.8	4.2
Ethanol	313–343	−2.05	630	1.1	5.2
Propanol-1	313–343	−1.95	767	1.9	6.4
Butanol-1	313–343	−2.25	996	3.0	8.3
Pentanol-1	318–343	−2.21	1130	4.8	9.4
meta-Cresol	303–343	0.94	111	3.7	0.9
Acetone	303–343	1.23	−592	0.5	−4.9
Acetonitrile	303–343	0.60	−470	0.4	−3.9
Diethyl ether	303–343	1.94	−569	1.0	−4.7
1,4-Dioxane	313–343	0.95	−525	0.5	−4.4
Tetrahydrofuran	303–343	1.41	−848	0.2	−7.1
Dichloromethane	303–343	0.61	−110	1.3	−0.9
Trichloromethane	303–343	1.59	−18	4.6	−0.2
Pyrrole	303–343	1.37	−824	0.2	−6.8

[a] Standard uncertainties u are $u(a) = 3\%$; $u(b/K) = 3\%$ $u(\gamma_i^{\infty}) = 3\%$.