^{2}H NMR study of hydrogen bond dynamics and phase transition in a model ionic liquid electrolyte

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^{2}H NMR method is a versatile tool that allows probing dynamics and phase behaviour in solid state. This method has been successfully utilized in various systems ranging from zeolites to proton conductors and polymers. Recently, we have developed a robust approach for gaining access to the structure and dynamics in liquid, supercooled and crystallized protic ionic liquids (PILs) by using the solid state ^{2}H NMR line shape and spin relaxation analysis. Herein, we exploit this approach to perform a comprehensive solid state ^{2}H NMR study of the PIL over a broad temperature range of 133-436 K, delivering information about the hydrogen bond dynamics and phase transition in the model ionic liquid electrolyte triethylammonium bis(trifluoromethanesulfonyl)imide [TEA][NTf$_2$].Deuterium is located in the N-D group of [TEA] cation so we can directly follow the dynamics of hydrogen bond between cation and anion. ^{2}H NMR spectra line shape at 133-223 K consists of two Pake doublets with notably different deuterium quadrupole coupling constants (DQCC) $Q_{Ia} = 172 - 175$ kHz and $Q_{Ib} = 144 - 145$ kHz. It indicates at two possible ways of hydrogen bond formation. Density function theory (DFT) calculations allowed determining the geometry of ion pair responsible for these signals. In the 233-283 K temperature region the coexistence of liquid and solid state can be observed. We show that melting transition is governed by two sets of thermodynamic parameters. For the initial process below 238 K $\Delta H_1^{\ominus} = 110 \pm 20$ kJ mol^{-1}, close to the second melting transition we obtained $\Delta H_2^{\ominus} = 22 \pm 5$ kJ mol^{-1}, indicating that less energy is required to reach the second melting transition. In order to probe motional behavior of [TEA][NTf$_2$] we measured the deuteron spin-lattice $(T_1)_D$ and spin-spin $(T_2)_D$ relaxation times of the N–D molecular vector for the isotropic and anisotropic components. From fitting the temperature dependence of spin relaxation times, we determine the geometry, activation barriers and rates of motions exhibited by the [TEA] cation.

We compare our results with previously reported data regarding ionic liquids with anions of varying strength: [TEA][OTf] and [TEA][OMs]. Our results prove that the stronger hydrogen bonds between cation and anion lead to the lower enthalpy change between solid and liquid state, higher activation barrier of tumbling motion and lower amplitude of librational motion.