

Ion-Pair Formation of the Ionic Liquid [EMIM][NTf₂] as a Function of Temperature and Concentration

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IR spectroscopic results are presented for neat [EMIM][NTf₂] as well as solutions in DCCl₃ up to 62 percent of DCCl₃ in the range of 2800 to 3300 cm⁻¹. Spectra have been deconvoluted by using Voigt functions. The results of this procedure clearly indicate, that two kinds of ion pairs exist with hydrogen bondings in the C2 and in the C4/C5 position competing with H-bondings in network structures including at least 2 molecules of [EMIM][NTf₂].

Ion pair formation can be assigned to stretching frequencies of H-bonded CH groups in the C2 and the C4/C5 position at 3105 cm⁻¹ and 3155 cm⁻¹ respectively while network bonded CH frequencies appear at 3130 cm⁻¹ and 3175 cm⁻¹ respectively. The formation of ion pairs is clearly favoured at higher temperatures in both the neat liquid and the DCCl₃ solutions. Ion pairs are also preferred in comparison to network structure with decreasing concentration of [EMIM][NTf₂] in DCCl₃.

In general it has been found, that as soon as ion pairing becomes dominating the equilibrium between ion pairs in the C2 position and the C4/C5 position is shifted to the C2 ion pairs.

The spectroscopic results and their interpretation are strongly supported by DFT-calculations (B3LYP, 6-31G* basis set) of ion pairs and network structures containing up to 4 ionic species.

The red shift effect of CH-stretching frequencies in the two kind of ion pairs compared to those in the network structure has been confirmed by the theoretical results.