Interplay between Magnetic Relaxation and Molecular Dynamics in Ionic Liquids

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Ionic liquids are increasingly popular in the scientific literature. They exhibit a wide range of distinctive features. Considerable attention has been devoted to their role in green chemistry, where they are explored as environmentally friendly solvents and catalytic media, as well as to their prospective use in energy storage technologies. The present study focuses on a series of EMIM and OMIM ionic liquid compounds that share common anions (BF_4^-, Cl^-) and differ in the length of their alkyl substituents.

The primary aim of this work was to examine the molecular dynamics of these systems. NMR spectroscopy was applied in combination with the continuous-wave (CW) NMR technique. NMR investigations were conducted on the nuclei ^1H and ^{19}F using a Bruker CXP spectrometer operating at 200 MHz. Measurements were performed over a temperature interval from 90 to 400 K. To extract the activation parameters associated with the proposed molecular motions, spin-lattice relaxation times (T_1) were determined using an approach grounded in statistical models of magnetization transfer within spin systems. During the experiments, free induction decay (FID) signals were recorded and analyzed across the entire experimentally accessible temperature range. These investigations and analysis were extended by the continuous-wave (CW) NMR technique. It was used to determine the reduction of the second spectral moment (ΔM_2). Changes in M_2 provided complementary information on the extent of the averaging of dipolar interactions caused by molecular and segmental motions, allowing a direct assessment of local mobility in the solid (static amorphous) and highly viscous phases. Moreover, temperature dependent measurements of M_2 allowed identification of the onset of motional narrowing effects associated with alkyl chain reorientations and conformational dynamics, particularly for compounds with longer substituents. The application of the analysis method of ΔM_2 served as an independent indicator of dynamic transitions, supporting the interpretation of relaxation processes derived from relaxation times T_1 and the results of differential scanning calorimetry (DSC) [1].

All results indicate that for systems with longer alkyl chains, the dominant relaxation mechanism arises from anisotropic rotation of methyl groups coupled with trans-gauche conformational transitions of the CH_2 units, while at higher temperatures, motions of individual molecular groups become increasingly pronounced.

References:

[1] Wrembel W., Fojud Z., “Investigating dynamic processes in molecular charge carriers by means of NMR spectroscopy and differential scanning calorimetry”, The 21st European Magnetic Resonance Congress EUROMAR 2025, 6–10 VII 2025, Oulu, Finland, Book of Abstracts p.233, poster no.103 , poster and oral presentation