Studies of Ionic Liquids Using Nonlinear EPR Spectral Fitting

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Our laboratory has used nonlinear spectral fitting in EPR spectroscopy for more than three decades because it significantly enhances the precision and sensitivity of spectral analysis. This approach enables highly accurate determination of EPR parameters, including hyperfine coupling constants and intrinsic Lorentzian linewidths, while correcting for inhomogeneous and modulation-induced broadening. As a result, it not only improves measurement sensitivity but also provides access to spectral parameters that are difficult or impossible to obtain using conventional analysis methods. Here, I present two studies that demonstrate the power of nonlinear spectral fitting for investigating ionic liquids.

1) Rotational Dynamics of Nitroxide Probes in Ionic Liquids

EPR measurements of the nitroxide probes Frémy's salt (FS) and di-tert-butyl nitroxide (DTBN) in imidazolium-based ionic liquids show that their rotational dynamics are governed primarily by charge rather than by their similar size and shape [1]. The negatively charged FS resides within the polar ionic network, where its rotational motion becomes increasingly anisotropic as the cation alkyl chain length increases. In contrast, the neutral DTBN preferentially partitions into the nonpolar alkyl domains and undergoes nearly isotropic rotation. Although both probes exhibit the same viscosity-controlled activation energy for rotational motion, their distinct local environments produce markedly different rotational behavior and hyperfine coupling constants. These results provide direct insight into the nanoscale organization and heterogeneous domain structure of ionic liquids.

2) Phase Behavior of Paramagnetic Ionic Liquids

EPR spectroscopy was also used to investigate the phase behavior and magnetic interactions of the paramagnetic ionic liquids [Emim][$FeCl_4$] and [Bmim][$FeCl_4$] [2]. By analyzing exchange-narrowed EPR linewidths, nonlinear spectral fitting distinguished crystal polymorphs, phase transitions, and glass formation, and enabled estimation of the superexchange coupling between Fe^{3+} ions. In [Emim][$FeCl_4$], two crystal polymorphs with different superexchange coupling strengths were identified below the solid–solid transition, whereas [Bmim][$FeCl_4$] underwent a glass transition rather than crystallization. These findings demonstrate that EPR spectroscopy, combined with nonlinear spectral fitting, is a highly sensitive tool for probing crystal polymorphism, magnetic exchange interactions, and phase transitions in paramagnetic ionic liquids.

References:

[1] M. H. O'Brien et al., J. Mol. Liq. **404**,124994, (2024)
[2] Y. F. Lencina Wendt et al., J. Chem. Phys. **163**, 174505, (2025)