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Chemical Exchange Processes Studied by 95 GHz 2D-ELDOR

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Exchange processes which include conformational change, protonation/deprotonation, binding equilibria etc. are routinely studied by various 2D NMR techniques, e.g. EXSY, ZZ-exchange, CEST. In these techniques the information about exchange of nuclei between environments with different NMR parameters is obtained from the cross-peak development. Cross-peaks due to chemical exchange have been previously seen in EPR, but for most common EPR probes their observation and analysis at low EPR frequencies is difficult because the exchanging states are poorly resolved and their separation is comparable or less than their individual linewidths. With 2D ELDOR spectroscopy at 95GHz we benefited from the increased g-factor resolution to study chemical and physical exchange for protonation/deprotonation and partition equilibria of nitroxide radicals. The protonation/deprotonation process was studied for a pH sensitive imidazoline spin label, with both the relative ratio of exchanging states and the exchange rate controlled by the composition and the concentration of the buffer solution respectively1. This allowed for reliable assignments of cross-peaks related to chemical exchange and for separating them from cross-peaks emerging from Heisenberg exchange and Electron-Nuclear Dipole (END) interactions. The exchange rate obtained from the cross-peaks is in good agreement with the changes in relaxation times of the exchanging states derived from the same 2D ELDOR experiment and other EPR experiments. For a totally different system of a nitroxide radical partitioning between polar and non-polar environments in microemulsions and multilamellar lipid vesicles we also demonstrated the cross-peak development owing to physical exchange between different phases and measured its rate. These experiments were carried out on ACERT's newly rebuilt 95 GHz 2D ELDOR spectrometer.

1Khramtsov V, Bobko A, Tseitlin M, Driesschaert B. Exchange Phenomena in the Electron Paramagnetic Resonance Spectra of the Nitroxyl and Trityl Radicals: Multifunctional Spectroscopy and Imaging of Local Chemical Microenvironment. Anal Chem. 2017 89(9):4758-4771

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