

ESR-Spectroscopy in Ionic Liquids: High Pressure Investigations on the Rotational Dynamics of some Nitroxides

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Ionic liquids (ILs) are molten salts of mainly organic cations and inorganic or organic anions, liquid at room temperature. They are of interest, not only from scientific point of view but also for chemical industrial productions. Environmental friendly industrial productions based on so-called “Green Chemistry” principles mainly use ionic liquids as solvent to avoid classical toxic organic solvents. But, few reports exist on ESR-spectroscopic investigations using ionic liquids as solvents. We would like to report on ESR-measurements using various nitroxides (TEMPO; TEMPOL and TEMPAMINE) in different ionic liquids. We have constructed a high-pressure system for use in electron spin resonance (ESR) spectroscopy. The apparatus allows the application of pressures of up to 100 MPa to solutions and with several key solvent properties (viscosity, dielectric constant, relaxation times, refractive index) being pressure dependent, reaction dynamics may be probed via pressure variations.

Rotational correlation times τ_{rot} : Using the high viscosity of ionic liquids, the rotational correlation times, τ_{rot} , of uncharged TEMPO-derivatives and of charged Fremy’s salt are measured as a function of temperature [1,2] **and** pressure [3]. Therefore, experimental values of both activation energies and activation volumes are obtained. The rotation correlation times vary between 54 and 1470 psec at 300 K. Activation volumes vary from 38.5-56.6 Å³. Within a temperature range of 280-380 K, the rotational tumbling is very well described by the Stokes-Einstein-Debye law. This study is distinguished from similar studies by the fact that proton super-hyperfine coupling constants could be resolved for all nitroxides in the ionic liquids by carefully optimizing the experimental details. As a consequence, many rotational correlation times reported here are smaller than those found previously. Furthermore, the temperature dependence of the nitrogen ESR coupling constants is reported and discussed in detail.

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[2] B.Y. Mladenova Kattnig, N.A. Chumakova, D.R. Kattnig, I.A. Grigorev, G. Grampp, A.I. Kokorin, *J. Phys. Chem. B*, **2021**, *125*, pp. 9235-9243.

[3] B.Y. Mladenova Kattnig, D.R. Kattnig, G. Grampp, *J. Phys. Chem. B*, **2022**, *126*, pp. 906-911.