

Investigating the temperature and solvent effects on the cyclohexadienyl radical in an ionic liquid

B. Taylor, P.J. Cormier, J.M. Lauzon, K. Ghandi*

Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada, E4L 1G8

Abstract: The cyclohexadienyl radical was studied in a novel green solvent; Tetradecyl-(trihexyl)phosphonium chloride ionic liquid (IL 101). Both the solvent and temperature effects on hyperfine coupling constants have been examined and compared to the literature. This was done through experimental muon techniques at TRIUMF National Laboratory in Canada as well as through ab initio calculations. The ionic liquid solvent effects were found to be consistent with other solvents, when assuming ionic liquids are made of ion pairs interacting with cyclohexadienyl radical. In ionic liquid the hyperfine coupling constants of the proton and reduced muon decreased linearly with increasing temperature. The analysis showed that the majority of this relationship is due to a vibrational effect, although the solvent density also plays a role. Assuming the vibrational motion of CHMu is not affected by ionic liquids, the temperature effect on the entropy of the system was determined to be negligible. The temperature coefficient of the reduced muon hyperfine coupling was larger than that of the proton in IL 101 due to the electronic effects of nearby ionic liquid molecules.