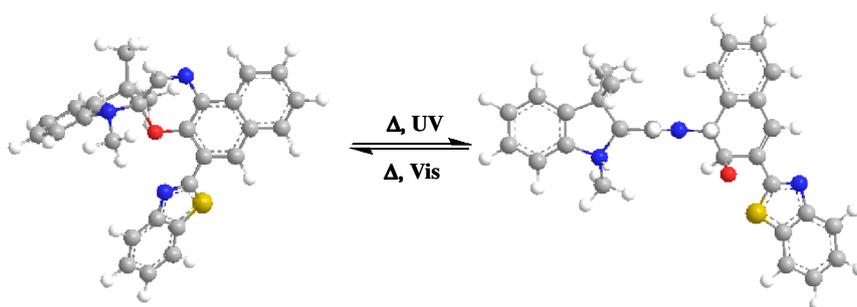


Investigating nano-structured domains within ionic liquids: the effect of cation change on thermal equilibrium and relaxation of spiroopyran and spirooxazine.

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The established belief that ionic liquids (ILs) behave as homogenous solvents such as that observed in molecular solvents has been challenged.^{1,2} Previous use of solvatochromic probe dyes has allowed for the traditional parameter of 'polarity' to be determined.³ These values were compared to the kinetics of the photochromic spirocyclic compounds spirooxazine (SO) and spiroopyran (SP). The nature of SO substituents limit the ability of hydrogen bond formation and so relies primarily on electrostatic interactions with the solvent system. Such an increase in solute freedom would be expected to increase the ability of the molecules to dissociate and migrate within the solvent system. A polarity-kinetic relationship for spirocyclic compounds has been established in molecular solvents with increasing polarity exhibiting decreased rates of thermal relaxation from the coloured merocyanine (MC) form to the spiro (SO/SP) form.⁴ However, thermal relaxation of SO in ionic liquids fails to present a correlation between polarity and kinetics. Kinetic studies were further enhanced by analysis of the relaxation process using thermodynamic parameters of activation. Previous studies have (primarily molecular modelling) proposed that ionic liquids possess a structured in-homogenous structure containing distinct areas of polar and non-polar regions.⁵ The probe dyes used to examine parameters such as hydrogen bonding (Kamlet-Taft) and polarity ($E_T(30)$) may only examine a particular region in the solvent. This means that the probe molecules may solvate in one region while compounds such as SO may interact in another region completely and therefore not allow for correlation of polarity to thermal relaxation rates observed. The closed form is a neutral compound exhibiting non-polar characteristics. MC, due to its zwitterionic nature, is in contrast highly polar. We believe that the size and ratio of polar to non-polar regions may be a critical factor in the process of SO thermal relaxation. Increasing non-polar regions may encourage the SO form by shifting equilibrium and encouraging migration and facilitate enhanced closure of MC within the solvent system. Thermal relaxation of SO may therefore allow for confirmation of the theory of IL structuring. Due to the large range of ILs possible, a correlation in structural effects and a quantifiable change may aid in a more detailed understanding of ILs and facilitate customisability of the liquids to meet specific polarity/solvation requirements.



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