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A Spectroscopic Analysis of Ionic Liquid Properties

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Abstract

The use of ionic liquids in chemical processes is becoming of increasing interest, due to the low volatility of ionic liquids, and the wide range of properties which they possess. The ability to select properties based on anion and cation choice is also desirable. As such, the development of a solvent reorganization energy scale incorporating both common organic solvents and ionic liquids is useful, as it can be used to determine appropriate ionic liquid replacements of common organic solvents for use in applications.

Raman spectroscopy studies have been performed on solutions of the solvatochromic Reichardt's dye in a selection of common organic and ionic liquid solvents. Due to the solvatochromism of Reichardt's dye, it behaves differently in solvents with differing properties. As such, the cross-sections of bands in Raman spectra associated with Reichardt's dye differ between solvents also. Modelling of these cross-sections enables solvent properties to be determined.

Absorption spectra were acquired of each sample, and resonance Raman spectra of each sample were recorded at a range of excitation wavelengths. After appropriate data treatment, the absorption and Raman cross-sections were determined, in order to enable the modelling of absorption and Raman cross-section profiles. The modelling of these profiles enabled the solvent reorganization energy of the organic solvents and ionic liquids to be determined, and a relative scale of solvent reorganization prepared.

Computational studies were performed in order to better understand the dynamics of Reichardt's dye in solution. The results from the studies were used to assign the vibrational modes of the Reichardt's dye to bands in the resonance Raman spectra.

From a solvent reorganization standpoint, it was found that common organic solvents may be replaced by ionic liquids of similar properties in applications where solvent volatility is an issue. In addition to this, the information obtained through the use of the solvent reorganization energy scale is able to be directly related to applications of ionic liquids involving electron transfer.

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Glossary of ionic liquid names

The names of ionic liquids are formed through the combination of the names of the cations and anions present. The acronyms for the cations and anions used in this study are listed below with the corresponding systematic name. The acronyms are used predominantly in this thesis for ease of comparison between ionic liquids.

Cations

BMIM 1-butyl-3-methylimidazolium

BMPY 1-butyl-3-methylpyridinium

BMMIM 1-butyl-2,3-dimethylimidazolium

Anions

PF₆ hexafluorophosphate

OAc acetate

TFSA bis(trifluoromethylsulfonyl)imide