

STUDIES OF ORGANIC SOLVENT POLARITIES USING IONIC LIQUIDS AS ADDITIVES

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Introduction: Ionic Liquids (ILs) are organic salts with an almost unlimited combination of cation-anion pairs which are liquid up to 100°C. Since they have no measurable vapour pressure they can be used as relatively environmentally benign media for a range of industrial processes and can be regarded as ideal substitutes of organic solvents due to their stability, nonvolatility and adjustable miscibility in many extraction processes.[1]

Reichardt [2] proposed a practical definition of the solvent polarity (later accepted by IUPAC [3]) as the “overall solvation capability (or solvation power) for (i) educts and products, which influences chemical equilibria; (ii) reactants and activated complexes (“transition states”), which determines reaction rates; and (iii) ions or molecules in their ground and first excited state, which is responsible for light absorptions in the various wavelength regions.”

A considerable amount of ionic liquids polarities measurements have been reported already. Different probes as well as measurement techniques have been used, but the most widespread technique explored has undoubtedly been the solvatochromism of betaine dye n^o. 30 (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate; Reichardt’s dye) studied by UV/Vis spectrometry. [4]

In the present work, we have investigated how the polarity of common organic solvents such as acetonitrile, ethanol, iso-propanol and chloroform is affected by the presence of small quantities of ionic liquids (maximum 10 µl). This could be a viable alternative to the employment of pure ionic liquids, due to their high cost and known ecological impact.

Experimental: All ionic liquids used in this work are from Solchemar (>98% purity), except 1-ethyl-3-methyl-imidazolium ethylsulfate ([EMIM][EtSO₄], trade name ECOENG 212) and 1-ethyl-3-methyl-imidazolium 2-(2-methoxyethoxy)-ethylsulfate ([EMIM][MDEGSO₄], trade name ECOENG 21M), which were purchased from Solvent Innovation (≥98% purity), and trihexyltetradecylphosphonium tetrafluoroborate ([C₆]₃C₁₄P][BF₄]) which was purchased from Fluka (purum ≥95%). The solvents used were ethanol, acetonitrile, isopropanol and chloroform (Pro analysis or HPLC grades).

Experimental method: Solutions of 20 mg betaine dye no. 30 (Sigma-Aldrich, >90%) in 100 mL of solvent (ethanol, acetonitrile, isopropanol or chloroform) were prepared as stock solutions for the measurements. From these stock solutions, 2,4 mL were placed in a

quartz cell of 10 mm path length. The appropriate volume of the ionic liquid to be measured was added and the cell was agitated for complete dissolution. Measurements were performed either in a Perkin Elmer Lambda 35 UV/Vis Spectrometer or in a UV/Vis Cary 100. The results are the average of at least two measurements.

Results and discussion: It was observed for all the cases tested that acetonitrile polarity increases with the addition of ionic liquid. Specifically, acetonitrile polarity increases with the addition of ionic liquids which have [BMIM] as the cation in the sequence [Cl] $<$ [PF₆] $<$ [BF₄] $<$ [NTf₂], which is in accordance with the expected polarity of these anions. Surprisingly, though, the anion [DCA] presents an effect in acetonitrile polarity lower than that of [Cl]. This might be due to the structural similarities of acetonitrile and the dicyanamide anion, which would lead to a lesser disruption of the supramolecular arrangement of the solvent.

As for the [OMIM] cation, polarity of acetonitrile is found to increase in the sequence [PF₆] $<$ [BF₄] \approx [Cl] $<$ [DCA] $<$ [NTf₂]. This effect is probably explained by a stabilization of the charge distribution between the anion and the cation, due to the longer alkyl side chain in the imidazolium ring of [OMIM]. Figure 1 shows the anion effect in the case of BMIM and OMIM cations compared with pure acetonitrile (in E_T^N values).

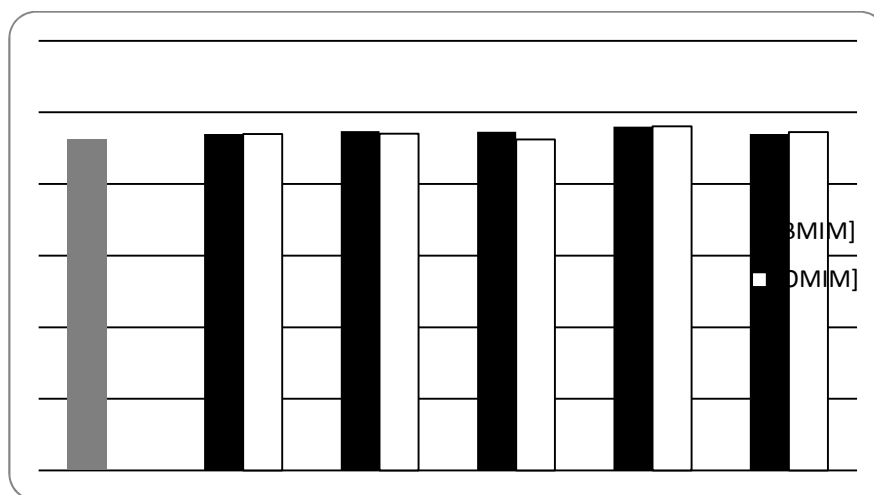


Figure 1. Anion effect in E_T^N values of acetonitrile.

Additional studies in the case of acetonitrile were performed using others ionic liquids as additives based on methylimidazolium, phosphonium, ammonium and guanidinium cations combined with several inorganic and organic anions. Also, ethanol, iso-propanol and chloroform were used as organic solvents in these polarity studies.

Conclusions: These studies showed that some ionic liquids can be used as additives (in small quantities) in order to influence the polarity of polar (e.g. alcohols) or apolar (e.g. nitriles and halogenated compounds) organic solvents. According with cation-anion combinations of ionic liquids, it will be possible to improve the solubility of some solutes in specific organic solvents as well as their further separation and purification processes.

References:

1. N. V. Plechkova, K. R. Seddon; Applications of ionic liquids in the chemical industry; *Chemical Society Reviews*, 37 (2008) 123–150.
2. C. Reichardt; Empirical Parameters of the Polarity of Solvents; *Angewandte Chemie International Edition*, 4 (1965) 29–40.
3. P. Muller; Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994); *Pure and Applied Chemistry*, 66 (1994) 1077–1184
4. C. Reichardt, Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium N-phenolate betaine dyes, *Green Chemistry*, 7 (2005) 339–351.