POSTER SUMMARY

PREPARATION OF THREE NOVEL IONIC LIQUIDS FOR THE DISSOLUTION OF CELLULOSE

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Abstract

The full potential of sugarcane bagasse has not been fully exploited, with the main usage in South Africa being for providing energy in sugar mill operations, and portions being utilised for paper products, animal feed and furfural production. The dissolution and subsequent reactions of cellulose from sugarcane bagasse is a possible future application of ionic liquids (ILs), which are more environmentally-friendly solvents that can also be used as reaction media. Such use of ILs is aimed at the production of value-added products from the abundant bagasse substrate. This work describes the synthesis of a starting compound (1-allyl-3-methylimidazolium bromide) and subsequent preparation and characterisation of three novel organic ILs (1-allyl-3-methylimidazolium lactate, 1-allyl-3-methylimidazolium acetate and 1-allyl-3-methylimidazolium salicylate) because of their potential for cellulose dissolution. Preliminary tests showed that, although the ILs are able to dissolve cellulose, the presence of water limited cellulose dissolution.

Keywords: ionic liquid, cellulose, synthesis, analysis, bagasse, byproducts

Introduction

An ionic liquid (IL) is a molten salt comprising a cation with a poorly coordinated anion (Kim *et al.,* 2008). Since their development in 1948 (Wilkes, 2002), ILs have become increasingly popular in research fields and industrial applications because they are less toxic than most organic solvents, and also because of their unique physical and chemical properties (Kim *et al.,* 2008). Moreover, these properties can be manipulated fairly easily through careful selection of the ionic couple of the IL (Cardiano *et al.,* 2008). Favourable properties of ILs include their negligible vapour pressure, high thermal and chemical stability, non-flammability, good solvating properties and highly polar nature. Unfavourable properties include residual halogen and disposal issues for halogenated ILs (Wasserscheid and Welton, 2007; Mallakpour and Taghavi, 2008).

Factors that influence a compound's ability to act as a solvent include its structure, its hydrogen bond accepting or donating ability and its polarity (Huddelston *et al.,* 2001). Due to their ability to solubilise synthetic polymers and biomacromolecules (Fukaya *et al.,* 2006), Swatloski and his coworkers found that the dissolution of cellulose in 1-butyl-3-methylimidazolium based ILs with various inorganic anions is possible (<25% (m/m)) (Swatloski *et al.,* 2002; Fukaya *et al.,* 2006). Current research on this topic looks into the synthesis of ILs with various organic anions and tests their solvating power on cellulose (Fukaya *et al.,* 2006; Pernak, 2003). This move came about with the aim to make these ILs greener (by removing the halogen component) and to develop innocuous solvents for the chemical processing and modification of biomacromolecules (Fukaya *et al.,* 2006).

This poster summarises the synthesis of the precursor halogenated IL (1-allyl-3-methylimidazolium bromide, amimBr) and subsequent conversion to one of three organic-based ILs, namely amim-lactate (amimLac), amim-acetate (amimOAc) and amim-salicylate (amimSal), using two methods developed in-house. Each ionic liquid synthesised was structurally elucidated by techniques including proton nuclear magnetic resonance (HNMR) spectroscopy and Fourier-Transform infrared (FTIR) spectroscopy. Furthermore, the IL's thermodynamic and some physical properties were evaluated, including heats of combustion, refractive indices, viscosities and impurities. Finally, the products were subjected to a preliminary solubility test on cellulose from filterpaper (which was used as a model compound) to assess the IL's solvating properties and future application using sugarcane bagasse as a substrate for the production of value-added products.

Methods

Synthesis of amimBr
AmimBr was synthesised without the use of a solvent by combining 1-methylimidazole with 3-bromopropene under an inert atmosphere at -10ºC to -15ºC in a 1.00:1.25 molar ratio. The amimBr was washed with diethyl ether and dried under vacuum before derivitisation. The product was confirmed through spectroscopic analyses.

Synthesis of amimLac and amimOAc
For the lactate and acetate derivatives an ion exchange technique was employed to first derivatise the precursor amimBr to an intermediate amim-hydroxide (amimOH). Thereafter, a potentiometrically monitored neutralisation reaction of the amimOH with lactic and acetic acid to produce amimLac and amimOAc, respectively, was conducted. The product was purified, dried and confirmed as described for amimBr.

Synthesis of amimSal
The salicylate derivative was produced without the use of solvent. Salicylic acid and amimBr were added to a flask in a 1:1 ratio, with stirring (24 hours) under an inert atmosphere at 50ºC. The biphasic product mixture could not be separated or purified and was not subject to any physical tests. Nevertheless, the presence of amimSal was confirmed through spectroscopic analysis.

Spectroscopic analyses of products
Structural analyses were done using HNMR and FTIR techniques. The HNMR analyses were measured against tetramethylsilane on a Bruker AMX spectrometer operating at 400 mHz. The FTIR analyses were done using a Perkin Elmer Precisely attenuated total reflectance (ATR) spectrometer.

Thermodynamic and physical properties
The average energy of combustion and molar empathy of the ILs were determined by bomb calorimetry. The viscosities were measured on a viscometer and the refractive indices were recorded with a refractometer.

Impurities analysis

The water content was determined on vacuum dried samples by Karl Fischer titration whilst the residual bromine in the derivitised ILs was measured by potentiometry.

Cellulose dissolution

Vials containing ~1 g (±10^{-5} g) of IL were each placed in a thermostat controlled ultrasonic bath and allowed to equilibrate to 35.5ºC. To each of the heated samples ~2.00 mg of cellulose was added. The level of dissolution of the cellulose was monitored by inspection at intervals. After an hour under these conditions, the samples were moved to a water bath and kept at 70°C with occasional agitation. Portions of cellulose (2.00 mg) were added to samples where complete dissolution of the initial cellulose was observed.

Results and Conclusions

The successful synthesis and purification of amimBr, amimLac and amimOAc were confirmed by the HNMR and FTIR analyses. Although the amimSal product could not be physically separated from unreacted amimBr and salicylic acid, the spectroscopic analysis on the product solution revealed that amimSal was synthesised. The three successfully synthesised ILs were tested to determine their physical properties, impurities and cellulose dissolving potential. The results outlined in Table 1 reveal that the presence of a high concentration of water (above 1%) (Swatloski *et al.,* 2002) restricted the aminBr from dissolving any cellulose, whilst amimLac and amimOAc were severely limited to dissolving less than 0.4% (m/m) cellulose. Further work is required to develop an improved method to synthesise amimSal, and improvements in all methods are required to reduce moisture content in these novel organic ILs. The aim of such work would be to show that the dissolution and subsequent reactions of cellulose from sugarcane bagasse is a viable application of ILs.

Table 1. Summary of results for the isolated ionic liquid products.

Parameter	amimBr	amimLac	amimOAc
Molar yield (%)	99.7	68.1	90.8
Percentage total impurities (%)	2.7	30.9	5.2
Average energy of combustion (MJ kg^{-1})	20.48	25.07	24.79
Molar enthalpy (Δ^{U}_{m}) (kJ mol^{-1})	4160	5323	4519
Viscosity (Pa s)	0.936[x] 0.296[y]	0.214	0.296
Newtonian factor	0.95[x] 0.97[y]	1.00	0.97
Average refractive index (n_D^{25})	1.5692	1.5064	1.5156
Average water (%)	2.7	3.4	4.9
Residual bromine (%)	N/A	1.06	1.05
Total mass percent cellulose dissolved (%)	0.0	0.2 – 0.4	0.2

[x] amimBr dry

[y] amimBr wet; was removed from the oven a week prior to aminBr dry, and sealed in a pill vial with a polyethylene cap

REFERENCES

Cardiano P, Minea PG, Neri F, Lo Schavo S and Piraino P (2008). A new application of ionic liquids: Hydrophobic properties of tetraalkylammonium-based poly(ionic liquid)s. *J Mater Chem* 18: 1253-1260.

Fukaya Y, Sugimoto A and Ohno H (2006). Superior solubility of polysaccharidesin low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates. *Biomacromolecules* 7(12): 3295-3298.

Huddelston JG, Visser AE, Reichert WM, Willauer HD, Broker GA and Roger RD (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry* 3: 156-164.

Kim J, Hayashi S, Onoda M, Sato A, Nishimura C, Mori T and Honma I (2008). New organic-inorganic crystalline electrolytes synthesised from 12-phosphotungstic acid and the ionic liquid [BMIM][TFSI]. *Electrochimica Acta* 53: 7638-7643.

Mallakpour S and Taghavi M (2008). Microwave heating coupled with ionic liquids: Synthesis and properties of novel optically active polyamides, thermal degradation and electrochemical stability on multi-walled carbon nanotubes electrode. *Polymer* 49: 3239-3249.

Pernak J (2003). New ionic liquids with organic anions. *Polish Journal of Chemistry* 77(8): 975-984.

Swatloski RP, Spear SK, Holbrey JD and Rogers RD (2002). Dissolution of cellulose with ionic liquids. *J Am Chem Soc* 124: 4974-4975.

Wasserscheid P and Welton T (2007). *Ionic Liquids in Synthesis.* Second Edition. Wiley-VCH Publishers. USA. pp. 371-373, 388.

Wilkes JS (2002). Ionic Liquids in Perspective: The Past with an Eye Toward the Industrial Future. pp 214-217 In: RD Rogers and KR Seddon (Eds). *Ionic Liquids: Industrial Applications for Green Chemistry*. ACS Symposium Series 818, American Chemical Society, Washington, USA.