NIR spectroscopy and chemometrics for ionic liquids: lignocellulosic biomass dissolution

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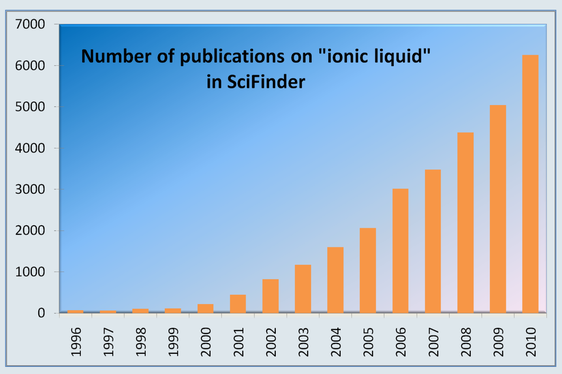
Introduction

The dissolution in ionic liquids (IL, [1]) is a new, alternative technology to disrupt the complex fibre network of lignocellulosic biomass at comparatively mild conditions [2]. Its three main compounds – cellulose, hemicelluloses, and lignin – can be separated by simple addition of an anti-solvent; e.g., the addition of water immediately precipitates amorphous cellulose from the IL. Cellulose, hemi-celluloses, and lignin are interesting renewable sources for biofuels, chemicals, and biomaterials. In this preliminary study we investigate the applicability of NIR spectroscopy and chemometrics for quantifying the three main compounds of lignocelluloses in IL.

Ionic Liquids

- consist entirely of ions (salts)
- melting point < 100°C (liquid at room T!)
- negligible vapour pressure
- excellent thermal stability up to 400°C
- non flammable
- electrically conducting, magnetic
- increasing scientific relevance since 2000
- many interesting applications!
- "design" properties by ion combination



(Bio-)Polymer Processing
- solvent for regenerating cellulose (fibres, films)
- enabling technology for manufacturing cellulose
- **dissolution and separation of lignocellulosic biomass**

Chemical Processing
- reaction media, catalysts, solvents

Metal Processing
- electroplating (aluminum, chromium)
- electropolishing of metal surfaces

Electrochemistry
- high-performance electrolyte in lithium ion batteries
- solvent and electrolyte in solar cells

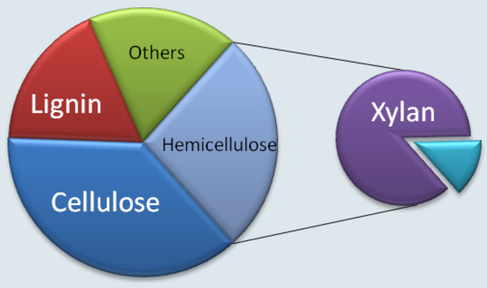
Engineering
- non-flammable hydraulic liquids
- high-performing lubricants
- liquid piston and gas compression

Separation Processes
- entrainer in extractive distillations (e.g., ethanol/water)
- extraction processes
- purification of gases

Functional Fluids
- antistatic additives, polymer additives
- catalysts
- reactive building blocks

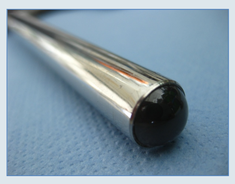
Lignocellulosic Biomass

- renewable plant material such as straw or wood
- main components: cellulose, hemicelluloses, lignin (see pie chart, approx. for straw)
- interesting renewable sources for biofuels, chemicals, biomaterials
- **problem**: complex fibre structure is recalcitrant against decomposition
- conventional technology for disruption: high T, high p, aggressive chemicals [3]
- "green" technology: dissolution in "EMIM-OAc", a non-toxic, biodegradable IL [4]



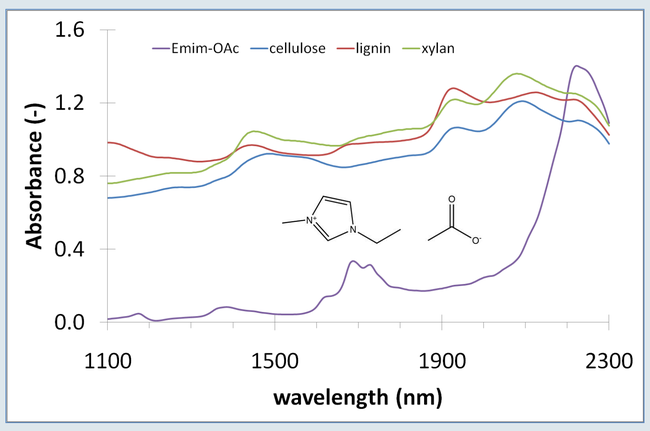
Experiments

- **Ionic liquid**: 1-ethyl-3-methylimidazolium acetate (EMIM-OAc > 98%, >2 €/g)
- **30 synthetic standards** of IL spiked with (a) cellulose *Avicel®* with 4-22 w-%, (b) lignin *"Kraft"* with 1.5-15 w-% or (c) hemicellulose *xylan from beech wood* with 3.2-20 w-%.
- **NIR spectrometer** (*Brimrose Luminar 5030*, AOTF), NIR absorbance measured at 1100-2300 nm (5 nm intervals, 241 variables).



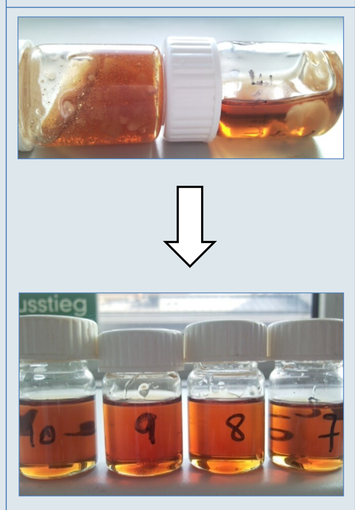
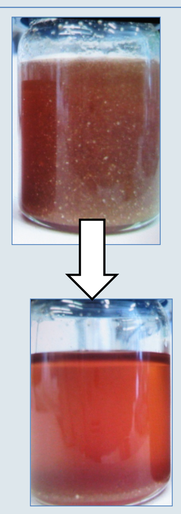
NIR transflectance probe with variable pathlength for liquid samples (up left); NIR diffuse reflectance probe for solid samples (up right).

Right: NIR spectrum and molecular structure of the used IL; NIR spectra of pure solid cellulose, lignin, and xylan.

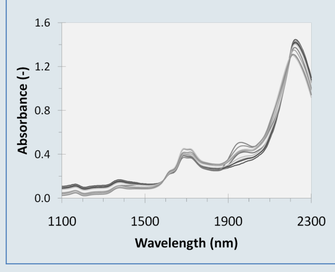
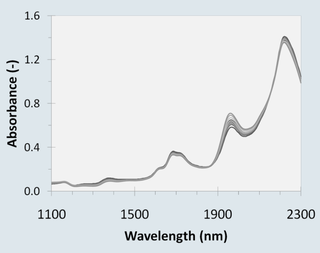
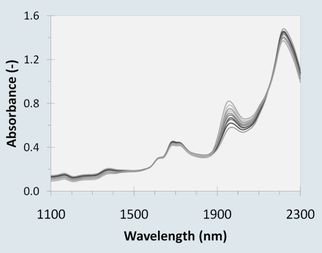


Dissolution of pure compounds in IL

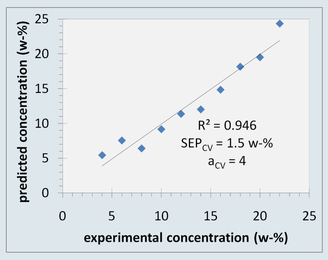
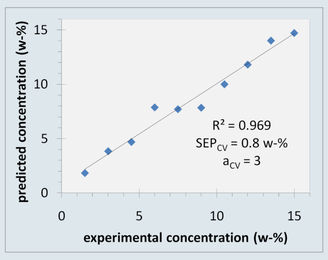
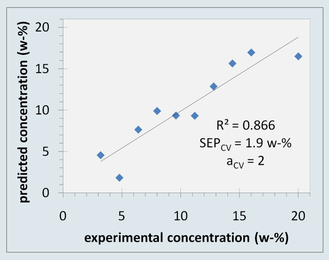
After mixing the pure compounds with the IL, it was necessary to dissolve the particles and agglomerations by ultrasound and temperatures 40-60 °C for 7-24 hours to obtain clear solutions.

Cellulose + IL	Lignin + IL	Xylan + IL
		

NIR absorbance spectra

Cellulose + IL	Lignin + IL	Xylan + IL
		

PLS regression models

Cellulose + IL	Lignin + IL	Xylan + IL
		

SEP$_{CV}$, standard error of prediction from leave-one-out cross validation
a$_{CV}$, number of PLS components
PLS-models with leave-one-out CV in Unscrambler [5].

Summary and Outlook

- Empirical models for the concentration of cellulose, lignin, and xylan in ionic liquid EMIM-OAc result in good prediction performance.
- In the next step, experiments will focus on multi-component mixtures of cellulose, lignin, and xylan in the ionic liquid.
- Good reference values for actually dissolved straw components in the IL is a limiting factor in PLS model building for industrial application.

References

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[3] J.Y. Zhu, X. Pan, R.S. Zalesny Jr., *Pretreatment of woody biomass for biofuel production: energy efficiency, technologies, and recalcitrance*, Appl. Microbiol. Biotechnol., 87, 847 (2010).
[4] P. Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm, J.P. Mikkola, *Dissolution of lignocellulosic materials and its constituents using ionic liquids—A review*, Ind. Crops Prod., 32, 175 (2010).
[5] Software The Unscrambler v 9.0, Camo Process AS, www.camo.no, Oslo, Norway, 2004.

Acknowledgements

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