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, hemicelluloses, 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

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

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).

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.

NIR absorbance spectra

PLS regression models

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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