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Lignocellulosic Biomass Dissolution and Fractioning Using Ionic Liquids as a Solvent

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Lignocellulosic biomass is a promising renewable resource for many different applications such as second-generation biofuels, chemicals and biomaterials. Its main components are cellulose, hemicelluloses (e.g., xylan), and lignin; they are combined in a complex fibre structure that is remarkably recalcitrant against decomposition. To disrupt this complex network and release single components, the conventional technologies apply high temperature, high pressure, and/or aggressive chemicals. In a new alternative method, an "ionic liquid" facilitates the dissolution of lignocellulosic biomass at comparatively mild conditions. Ionic liquids (IL) are a new class of salts with unique properties, such as low melting point (liquid at room temperature), negligible vapour pressure, and thermal stability. This work deals with the dissolution of synthetic cellulose, xylan and lignin as well as wheat straw in the ionic liquid EMIM-OAc. It further presents near infrared spectroscopy as promising analytical method to quantify dissolved components in ionic liquids. In addition, it introduces a stepwise procedure to fraction cellulose, xylan, and lignin from mixtures with ionic liquid. Based on these results, a promising procedure for fractioning the complex chemical components in lignocellulosic biomass can be derived.

1. Introduction

The dissolution in ionic liquids (IL, Kokorin, 2011) is a new, alternative technology to disrupt the complex fiber network of lignocellulosic biomass at comparatively mild conditions that is approximately 100 °C, ambient pressure, and without the use of other chemical agents (Zhu, 2008, Zhu et al., 2010, Sun, 2011). ILs can act as solvents and catalysts for a wide range of chemical applications. In particular, the IL 1-ethyl-3-methylimidazolium acetate (EMIM-OAc) has demonstrated to be an efficient solvent for lignocellulosic biomass; it is non-toxic, biodegradable, and thus a promising "green" candidate for industrial application (Sun et al., 2009, Mäki-Arvela et al., 2010).
Once dissolved in the ionic liquid, different compounds can be separated from the ionic liquid solution by precipitation. For cellulose, for instance, the precipitation is very simple, since the addition of water immediately precipitates amorphous cellulose from the IL (Sun et al., 2009). Apart from cellulose, the other main compounds of lignocellulosic biomass are hemicelluloses and lignin.

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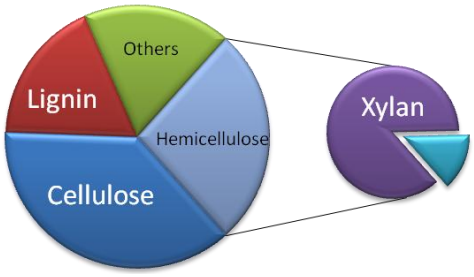


Figure 1: Approximate chemical composition of wheat straw; the three major compounds are cellulose, lignin, and hemicellulose. A large part of hemicelluloses consists of xylan.

In this study we investigate suitable anti-solvents that precipitate xylan and lignin from the ionic liquid solution. Xylan is chosen as representative for hemicelluloses. The aim is to set up a precipitation procedure for mixtures of cellulose, xylan and lignin. In addition, we develop calibration models for near infrared (NIR) spectra (Siesler et al., 2005) to analyse the concentration of the three main compounds of lignocelluloses in IL. In contrast to traditional methods, e.g., chromatography, NIR spectroscopy allows fast in-contact measurements in the IL without harming the measurement device.

2. Materials and Methods

2.1 Materials

The ionic liquid 1-ethyl-3-methylimidazolium acetate (proionic GmbH), often referred to as EMIM-OAc, has a purity of more than 98%, and is used as solvent. The solutes are cellulose Avicel® PH-101 (Fluka analytical Sigma-Aldrich), lignin alkali from Kraft process with low sulfonate content (Aldrich Chemistry Sigma-Aldrich), and xylan from beech wood with ≤ 10 % sulphate content (Roth). For each solute, 10 standard solutions with IL are prepared. These standards contain (a) 4-22 w-% cellulose, (b) 1.5-15 w-% lignin and (c) 3.2-20 w-% xylan. The dissolved compounds are precipitated with a suitable anti-solvent such as distilled water, ethanol or sulphuric acid.

2.2 Near Infrared (NIR) Spectrometer

The NIR spectrometer "Brimrose Luminar 5030" applies acousto-optic tuneable filter technology (AOTF) and is equipped with a transflectance probe that allows in-contact measurements. The NIR absorbance spectra are measured in the wavelength range of 1100-2300 nm at 5 nm intervals, which gives 241 NIR absorbance values per spectrum. NIR spectra, however, cannot be used directly for quantification, but have first to be calibrated with reference values. Since the concentration of the IL solutions are known by preparation, they can be used to build an empirical regression model y=f(X), with y being the concentration, and X comprising the NIR data. The regression models are computed by Partial-Least-Squares (PLS) regression and validated by leave-one-out cross-validation in software Unscrambler version 9.0 (Camo Process AS, Norway).

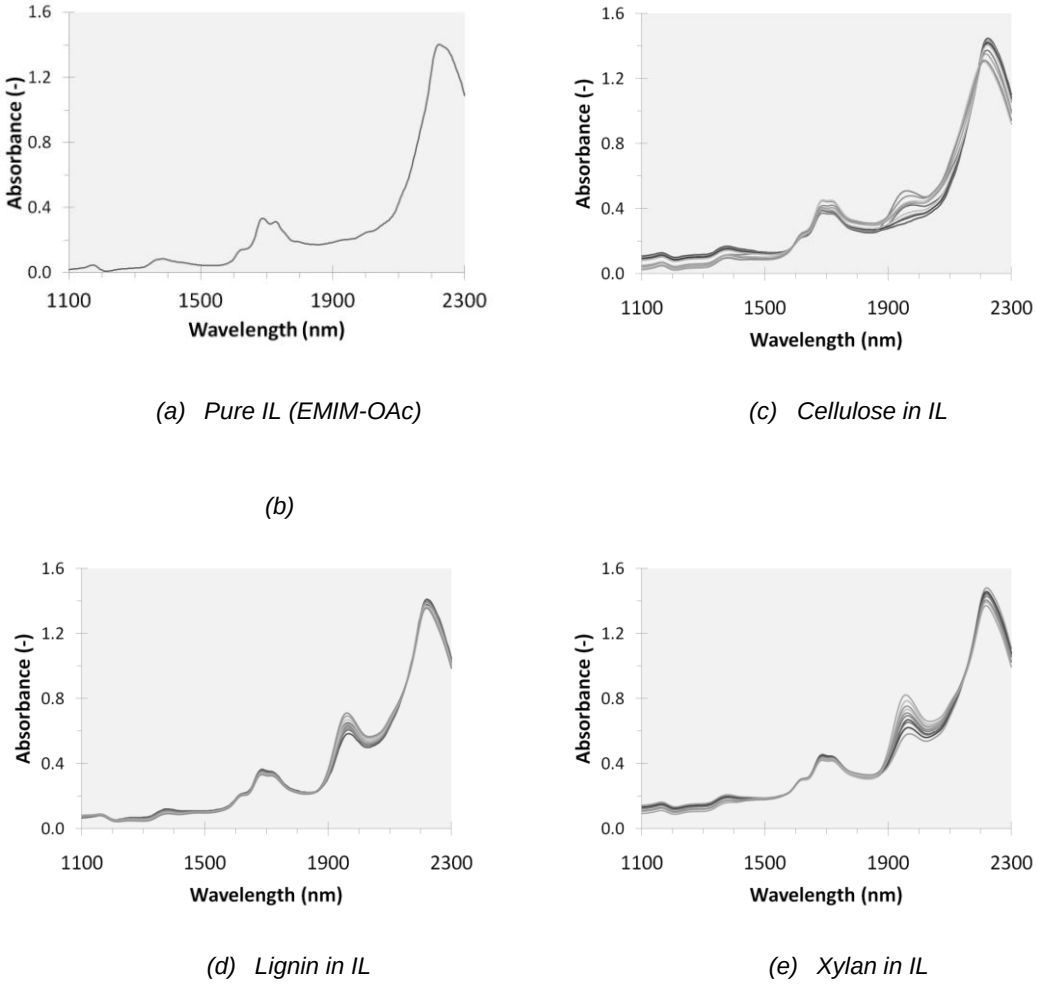
3. Results

3.1 Dissolution and quantification of synthetic compounds in ionic liquid

The three pure compounds, cellulose, xylan, and lignin, account for the main components of lignocellulosic biomass. The synthetic compounds are mixed, separately, with the ionic liquid, and typically form agglomerations. A clear solution can be obtained by ultrasound mixing and heating to 40-60 °C for 7-24 h, depending on the concentration.

The near infrared spectra of the pure ionic liquid as well as clear IL solutions with solvents are shown in Figure 1. It is typical for NIR spectra to exhibit broad absorbance peaks. EMIM-OAc, the used ionic

liquid, has the most prominent absorbance peaks around 2250 nm and 1650-1750 nm (Figure 1a); the peaks of varying height around 1900-2100 nm are due to different concentrations of cellulose, xylan, and lignin (Figure 1b,c,d). Despite the rather small differences in the spectra, the differences in concentration are in a range of 1.5-22 %-w/w.



(a) Pure IL (EMIM-OAc)

(c) Cellulose in IL

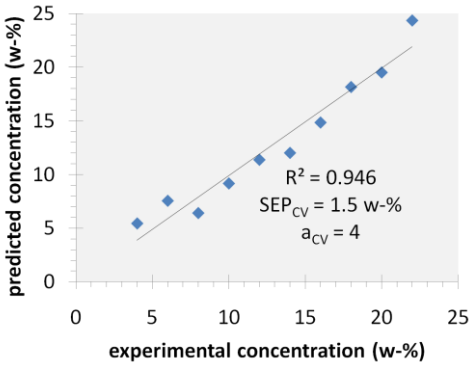
(b)

(d) Lignin in IL

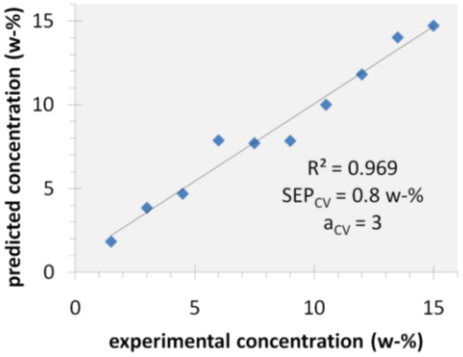
(e) Xylan in IL

Figure 2: NIR absorbance spectra of (a) clear IL solution EMIM-Oacs of > 98 % purity, and the same IL solution containing different amounts of (b) cellulose 4-22 w-%, (c) lignin 1.5-15 w-%, (d) xylan 3.2-20 w-%.

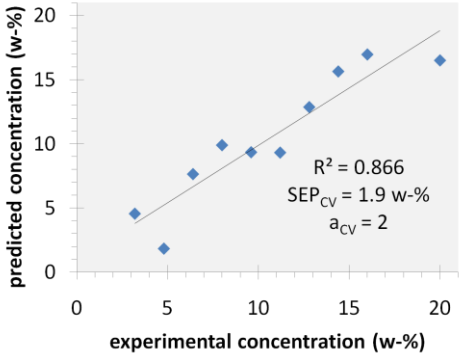
These spectra are successfully used in calibration models to predict the concentration of cellulose, xylan, and lignin in ionic liquid. The predicted values shown in Figure 2 are computed by PLS regression with leave-one-out cross validation. The squared Pearson correlation coefficient between experimental and predicted concentration is very high (R^2 > 0.9) for both cellulose and lignin, and indicates good model performance. Another statistical measure of model performance is the standard deviation of errors, SEP_{CV}; the errors are the differences between predicted and experimental values. Again, for cellulose and lignin the model performance is good with SEP_{CV} of 1.5 and 0.8 w-%, respectively. For Xylan, however, the model errors are slightly higher.



(a) Cellulose in IL



(b) Lignin in IL



(c) Xylan in IL

Figure 3: Predicted versus experimental concentration of (a) cellulose, (b) lignin, (c) xylan, in clear ionic liquid solutions. Predictions based on PLS regression with leave-one-out cross validation. The 45° line is the reference for a perfect model. R², squared correlation coefficient between predicted and experimental concentration; SEP$_{CV}$, standard deviation of prediction errors based on cross validation; a$_{CV}$, optimum model complexity (number of PLS components).

3.2 Precipitation of single synthetic compounds by anti-solvent

Cellulose precipitates from EMIM-OAc solution when water is added, and the solution is stirred vigorously. The solid cellulose phase can then be separated from the aqueous ionic liquid phase by centrifugation. For the precipitation of xylan, the addition of methanol works best, followed by ethanol as second-best of the tested anti-solvents, i.e., water, methanol, ethanol, sulphuric acid, and acetone. Eventually, ethanol is chosen as the standard anti-solvent for xylan, mainly because of the lower toxicity. The synthetic lignin dissolved in IL can be partly precipitated with water. This behaviour entails problems in the fractioning of cellulose and lignin, since both precipitate with the same anti-solvent. Another option with lignin is to lower the pH, which leads to sulphuric acid solution as alternative anti-solvent.

3.3 Precipitation of mixed synthetic compounds by anti-solvents

A mixture of cellulose, xylan, and lignin is dissolved in IL; each compound is to be fractioned in a separate step with the most appropriate anti-solvent. The stepwise procedure employs water for cellulose precipitation (step 1), ethanol for xylan precipitation (step 2), and aqueous sulphuric acid for lignin precipitation (step 3). In all steps, precipitation is enhanced by stirring at room temperature, and

then followed by a resting period of 24 h. Once a solid phase has formed, the sample is centrifuged; the solids are then separated from the liquid phase, and eventually washed and dried. The remaining liquid phase after step 1 contains an excess of water that is removed in a rotary evaporator, before step 2 is started. Likewise, the excess of ethanol after step 2 is evaporated.
After step 1, a mixture of cellulose and lignin is obtained as precipitate. Residues of ionic liquid can be removed from the solids by water, since neither cellulose nor lignin is soluble in water. Cellulose is subsequently cleansed from lignin by sodium hydroxide solution. After step 2, xylan precipitates from the ionic liquid solution as a caramel-like soft solid. After step 3, the solid, dark coloured lignin can be separated from the IL as the pH of the solution is strongly lowered by the acid. The basic pathway for precipitation appears to be reasonable, but the yields of single compounds are not yet satisfying (below 50 %).

3.4 Dissolution of wheat straw in ionic liquid

An amount of 1 g of wheat straw, with average particle size of 1 mm, is added to 20 mL of EMIM-OAc, and dissolves completely after 6 hours at 112 °C and vigorous stirring. The precipitation pathway developed for synthetic mixtures of cellulose, lignin and xylan in IL (see Section 3.3) is applied to the solution of wheat straw and IL. Each of the three precipitation steps yields a precipitate, but the theoretical yields are highly exceeded. The already indicated problems, such as coprecipitation of cellulose and lignin, do certainly increase when dealing with a natural raw material such as wheat straw. It stands to reason that the obtained precipitates do contain other compounds than cellulose, xylan, and lignin. It is also known that lignin behaves differently depending on its origin, e.g., lignin from beech wood versus lignin from wheat straw. A standard procedure for fractioning of lignocellulosic biomass from ionic liquid solutions will strongly depend on the support of appropriate analytical methods to get hold of the compounds present in both the liquid and the solid phase.

4. Conclusions

The ionic liquid EMIM-OAc, 1-ethyl-3-methylimidazolium acetate, can dissolve synthetic cellulose, xylan, and lignin as well as wheat straw under heating and stirring. With higher concentrations of solutes the viscosity increases considerably, so the solutions should be processed at elevated temperatures. The concentration of dissolved synthetic cellulose, lignin, and xylan in ionic liquid can successfully be determined by near-infrared spectroscopy in the investigated range of 1.5-22 % by weight. These positive results are only a start for further developing the NIR calibration models. A next step has to focus on complex ionic liquid samples that not only include lignocellulosic compounds, but also the anti-solvents such as water, ethanol, and sulphuric acid. This is not an easy task, since reliable reference concentrations have to be provided by an additional analytical method (e.g., NMR spectroscopy, HPLC, UV-spectrometry). These reference values are mandatory to build the calibration models for NIR spectra. A key requirement for an appropriate analytical method is that it should be insensitive to the presence of ionic liquid in the samples.
The found anti-solvents water, ethanol, and sulphuric acid manage to precipitate single compounds from complex synthetic mixtures in ionic liquid. However, the coprecipitation of lignin and cellulose, for instance, has to be minimized by a more suitable anti-solvent. More analytical research is necessary on the different types of lignin and hemicelluloses present in different classes of lignocellulosic material, in order to refine the fractioning scheme.

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