



Dissolution enthalpies of cellulose in ionic liquids

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ABSTRACT

In this work, interactions between cellulose and ionic liquids were studied calorimetrically and by optical microscopy. Two novel ionic liquids (1,5-Diazabicyclo[4.3.0]non-5-enium propionate and *N*-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethyl phosphate) and 1-ethyl-3-methylimidazolium acetate–water mixtures were used as solvents. Optical microscopy served in finding the extent of dissolution and identifying the dissolution pattern of the cellulose sample. Calorimetric studies identified a peak relating to dissolution of cellulose in solvent. The transition did, however, not indicate complete dissolution, but rather dissolution inside fibre or fibrils. This method was used to study differences between four cellulose samples with different pretreatment or origins.

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1. Introduction

Development of novel solvent systems for cellulose dissolution is a popular research topic. Due to strong inter- and intramolecular hydrogen bonding network cellulose does not dissolve in common molecular solvents. The traditional methods to process cellulose to textile fibres – i.e. the Viscose process, utilizing NaOH and CS₂ to dissolve cellulose, and the Lyocell process, using NMMO (*N*-methylmorpholine-*N*-oxide) – are costly, potentially hazardous and are not sustainable (Wang, Gurau, & Rogers, 2012). Ionic liquids (ILs) and aqueous alkali solvent systems are currently being studied for development of novel sustainable processes for cellulose modification and textile fibre production.

Molten salts capable of dissolving cellulose were first reported in 1934 in a patent by Graenacher, where alkyl pyridinium chlorides were used to solubilise cellulose allowing for homogenous modification (Graenacher, 1934). The distinction between molten salts and ionic liquids is that although both are composed of cation–anion pairs ILs have melting points below 100 °C. The cellulose dissolving capability of dialkyl imidazolium based ILs was demonstrated in 2002 by Swatoski, Spear, Holbrey, and Rogers

(2002). The best example for dissolving cellulose in this report was 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Fukaya and coworkers reported the first room-temperature ionic liquids (RTILs) that also possess the capability of dissolving cellulose, such as 1-ethyl-3-methylimidazolium formate ([emim][CO₂H]) (Fukaya, Sugimoto, & Ohno, 2006) or 1-ethyl-3-methylimidazolium dimethylphosphate ([emim][Me₂PO₄]) (Fukaya, Hayashi, Wada, & Ohno, 2008). However, 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) has been a ‘benchmark’ for cellulose processing ILs due to its excellent capability to dissolve cellulose while retaining relatively low viscosity. Recycling and purification of ILs is necessary for possible industrial applications. King, Asikkala, Mutikainen, Järvi, and Kilpeläinen (2011) introduced distillable ionic liquids (DILs) practically demonstrating the distillation of 1,1,3,3-tetramethylguanidinium propionate. However the viscosity of this IL is rather high for wide applications. It has been shown that the DIL 1,5-diazabicyclo[4.3.0]non-5-enium propionate ([DBNH][CO₂Et]) has similar temperature-viscosity correlation as [emim][OAc], which has a major influence on the practical cellulose dissolution capability (Parviainen et al., 2013). As such, ILs derived from alternative heterocycles can offer interesting properties, compared to imidazoliums.

The compact structure of cellulose fibres restricts the accessibility of chemicals on the surface of fibres. To enhance the reactivity of the pulps they are often subjected to various pretreatments

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to make them more accessible. Pretreatments aim to weaken or destroy the outermost layer of the native cellulose fibre that is the most difficult part of the fibre to dissolve. Some pretreatments, such as acid hydrolysis, may destroy the fibre structure almost completely.

Rheological studies have been conducted of polysaccharides and ionic liquids, but differential scanning calorimetry (DSC) studies of polysaccharide–IL interactions are less common. While there are no reports highlighting the dissolution process of cellulose in IL-system by DSC, starch–IL interactions have been previously studied (Mateyawa et al., 2013). Starch and cellulose are both polysaccharides composed of anhydroglucose units. In starch, majority of the anhydroglucose units are connected via $\alpha(1\rightarrow4)$ glycosidic bonds, while in cellulose they are linked with $\beta(1\rightarrow4)$ glycosidic bonds. Starch can also have branches linked with $\alpha(1\rightarrow6)$ bonds. Differences between starch and cellulose come not only from linear and regular structure of cellulose. In wood cellulose pulp, cell wall layers have different properties due different microfibril orientations and possible residual hemicelluloses and lignin. Starch processing for e.g. production of thermoplastic starch is widely studied (Jiménez, Fabra, Talens, & Chiralt, 2012) and solvents used to process cellulose have been studied for dissolution and modification of starch (Wilpiszewska & Szychaj, 2011). Mateyawa et al. (2013) studied phase transitions of starch in [emim][OAc]-water mixtures using DSC. Starch was mixed with solvent and heated from 25 °C to 120 °C, using 5 °C/min heating rate. Pure water or dilute [emim][OAc]-water solution as solvent resulted in gelatinization of starch and endothermic peaks in the DSC trace. High amount of IL or pure IL gave wide exothermic peaks from starch dissolution. Thermal transitions of starch in NMMO–water mixtures have been studied using DSC by Koganti, Mitchell, Ibbett, and Foster (2011). In high NMMO concentrations, dissolution was exothermic, and with high amount of water in the solvent, gelatinization and an endothermic peak were observed. Total dissolution enthalpy was described to consist of heat of melting and heat of mixing. Heat of melting was stated to be endothermic, but heat of mixing was exothermic and therefore the total heat exchange was exothermic.

In this work, the effect of the pretreatment, crystallinity of cellulose and IL-solvent used on the dissolution of cellulose was studied. Dissolution was followed step by step using optical microscope. Based on the obtained results a qualitative analysis of dissolution patterns and solvent properties was made. Thermal transitions relating to dissolution of cellulose was studied using differential scanning calorimetry.

2. Experimental

2.1. Materials

1-Ethyl-3-methylimidazolium acetate ([emim][OAc], >95%) was obtained from BASF. The water content was 0.15 wt% determined by Karl-Fischer titration. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) was purchased from Fluorochem Ltd. and trimethyl phosphate ($\geq 99\%$) from Sigma–Aldrich.

1,5-Diazabicyclo[4.3.0]non-5-enium propionate ([DBNH][CO₂Et]) was prepared as described by Parviainen et al. (2013). N-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethyl phosphate ([mDBN][Me₂PO₄]) was prepared using a Syrris® glass-jacketed reactor. For a 250 g batch of [mDBN][Me₂PO₄] the following method was used: 116.89 ml (0.946 mol) of DBN was charged to the reactor followed by flushing the headspace with argon gas. 110.71 ml (0.946 mol) of trimethyl phosphate was added to the DBN at 60 °C under argon atmosphere, as to keep the temperature below 80 °C during the exothermic reaction. The mixture was then heated to 75 °C where it was kept for one hour and then cooled

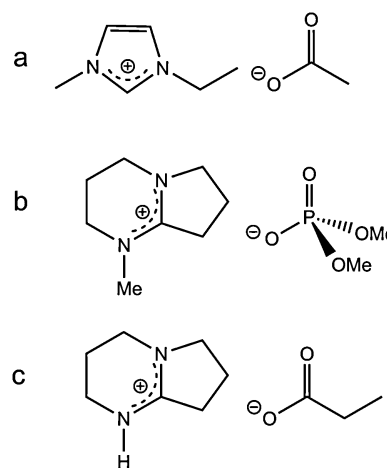


Fig. 1. Chemical structures of ILs used. (a) [emim][OAc], (b) [mDBN][Me₂PO₄] and (c) [DBNH][CO₂Et].

to room temperature. The product was an oil-like yellow liquid (Fig. 1).

Commercial dried spruce-pine dissolving grade sulphite pulp (cellulose content of 89.9%, viscosity 520 ml/g) from Domsjö Fabriker, Sweden was used in the study. Mechanical and enzymatic pretreatments were carried out at Tampere University of Technology (TUT) and at Finnish Technological Research Center (VTT). The pulp was mechanically shredded with Baker Perkins shredder machine (pulp consistency 20%) for 5 h. This mechanically treated pulp was denoted Pulp1. Enzyme- and mechanically treated pulp was prepared from Pulp1 by enzymatic treatment for 2 h, pH 5, 50 °C, 5% consistency, the enzyme dosage 0.5 mg/g. The enzyme used was a commercial endoglucanase rich enzyme preparation (FiberCare R, Novozym CGP20048). This pulp was denoted Pulp2.

To obtain a low crystallinity pulp, 0.5 g grinding milled (Wiley milled) pulp was weighed. 20 ml 70 wt% aqueous ZnCl₂ solution was added while stirring. The mixture was stirred for 2 h. Then the mixture was poured in water. The treated fibres were filtered to remove water and washed carefully. This pulp was denoted Pulp3. The pulp modification procedure was adapted from Mihriyan, Llagostera, Karmhag, Strømme, and Ek (2004).

Food-grade bacterial cellulose (coconut gel in syrup, nata de coco) was homogenized with a blender. To remove sugars, the homogenized gel was dialyzed through a regenerated cellulose tubular membrane (dialysis membrane nominal molecular weight cut-off of 3500 g/mol; Orange Scientific) against distilled water for 4 days. This sample is called nata de coco in this text.

ZnCl₂ was purchased from Sigma–Aldrich (purity $\geq 98\%$). The water used in the experiments was purified using a Millipore system (UHQ-water). Prior to DSC analysis and optical microscopy, the cellulose samples were freeze-dried.

2.2. Methods

2.2.1. Optical microscopy

Cellulose samples were studied with a polarized light microscope operated with a 10 \times /0.20 objective (100 \times magnification). The magnification was the same in all experiments; each picture shown represents 1 mm in height and width. For heating experiments under microscope, Mettler FP 82 hot stage was used to heat the sample between two glass slides. The heating rate was 5 °C/min.

2.2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed with Mettler Toledo STAR^e system equipped with a TGA850 thermobalance

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