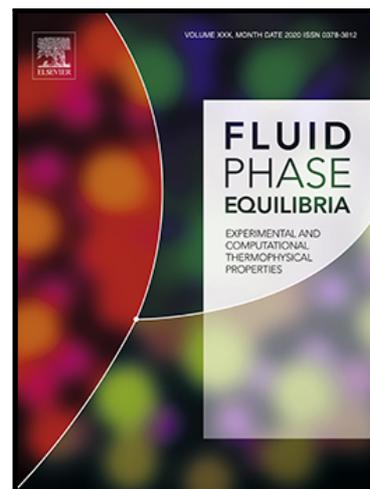


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Physico-chemical characterization of aqueous solutions of superbase ionic liquids with cellulose dissolution capability

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Superbase-based ionic liquids 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-enium acetate, [mTBDH][OAc], and 5-methyl-1,5,7-triaza-bicyclo-[4.3.0]non-6-enium acetate, [mTBNH][OAc], are good candidates to produce high performance cellulose fibres while presenting much easy spinnability and good recyclability, than the state-of-the-art ionic liquids. Nevertheless, the recovery of the IL from the aqueous spinning bath and its purification, which are both an economical and environmental necessity, are important aspects that are still not solved. Aiming to gather knowledge to recover and recycle superbase-ILs, the main goal of this work is the physicochemical characterization of the binary systems water + [mTBDH][OAc] or [mTBNH][OAc]. Measurements performed include solid-liquid equilibria, vapor-liquid equilibria, water activity, S_{λ}^{σ} solvatochromic parameters, densities, and viscosities. An experimental screening on possible hydrophobic extractants for the recuperation of the ionic liquids from aqueous solution was performed. Using butanol, an extraction efficiency of 37% for [mTBDH][OAc] was achieved. Better extraction efficiencies were achieved with chlorinated solvents, however, they seem to react with the ILs anion.

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ABSTRACT

Superbase-based ionic liquids 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-enium acetate, [mTBDH][OAc], and 5-methyl-1,5,7-triaza-bicyclo-[4.3.0]non-6-enium acetate, [mTBNH][OAc], are good candidates to produce high performance cellulose fibres while presenting much easy spinnability and good recyclability, than the state-of-the-art ionic liquids. Nevertheless, the recovery of the IL from the aqueous spinning bath and its purification, which are both an economical and environmental necessity, are important aspects that are still not solved. Aiming to gather knowledge to recover and recycle superbase-ILs, the main goal of this work is the physicochemical characterization of the binary systems water + [mTBDH][OAc] or [mTBNH][OAc]. Measurements performed include solid-liquid equilibria, vapor-liquid equilibria, water activity, S_{λ}^{σ} solvatochromic parameters, densities, and viscosities. An experimental screening on possible hydrophobic extractants for the recuperation of the ionic liquids from aqueous solution was performed. Using butanol, an extraction efficiency of 37% for [mTBDH][OAc] was achieved. Better extraction efficiencies were achieved with chlorinated solvents, however, they seem to react with the ILs anion.

Keywords

Superbase salt, ionic liquid, cellulose dissolution, liquid-liquid extraction, physicochemical properties

1. Introduction

In 2016, almost 100 million tonnes of textile fibres were produced globally and this number is expected to double by 2030 [1,2]. This growth allied to an increased environmental awareness has taken chemists to predict that man-made cellulose fibres will be the future of textile fibre market [3. 5]. Currently, these fibres are produced industrially from dissolving grade pulps using the traditional viscose or lyocell processes, which have severe drawbacks as environmentally hazardous solvents are used [5,6]. Researchers have then sought alternative sustainable technologies and solvents to produce these fibres, including the IONCELL-F process using ionic liquids (ILs) [2,7. 9].

Of the several hundred ILs identified as capable of dissolving cellulose [10] only a few are suitable to produce regenerated cellulose fibres, since ILs must be able to dissolve cellulose and allow regeneration upon addition of nonsolvent used to produce regenerated cellulose. Certain organic superbase-based ILs have shown good performance in cellulose dissolution, and some structures perform well in fibre regeneration to obtain high-performance textile fibres [11]. Preliminary fibre-spinning has identified [DBNH][OAc] as a key structure that allows for production of high performance fibres through the IONCELL-F process [12,13]. More recently, [mTBDH][OAc] and [mTBNH][OAc] were proposed as good candidates for the production of high performance fibres while presenting a negligible cellulose degradation under process conditions. Moreover, the superbase mTBD has a lower hydrolysis compared to DBN and the super base mTBN shows better stability in water, and the acetate salt is liquid at room temperature [14. 16]. These key findings opened an avenue to develop novel, hydrolytically stable ILs for textile spinning. However, serious questions remain such as the recyclability of these ILs.

After the regeneration of fibres, the spin bath contains mainly IL and water used as anti-solvent and possibly minor amounts of mono- and oligosaccharides from unregenerated cellulose, lignin fragments, non-polar substances, or other biomass components and in case of unstable ILs, some degradation products [17,18]. Recovery of IL and its purification is then a

complex challenge but also an economic necessity and compulsory from the environmental point of view.

The main IL recycling methodologies being studied are solvent distillation [16,19], IL distillation [11,12], extraction [20, 23], crystallization [24,25], and membrane separations [26,27]. The selection is mostly based on the ionic liquid physicochemical properties and its interaction with the solvent used in the cellulose precipitation, usually water [28].

An ideal IL recovery process should remove water and solutes that decrease process efficiency, require minimal additional or non-recycled reagents, and cannot result in significant IL degradation. Some solutions for the IL recovery have been proposed in the literature, such as liquid-liquid extraction [22,23]. This methodology is based on differences in the solubility of IL in two immiscible phases, allowing the regeneration and reuse of ILs. Polar solvents such as acetonitrile or dichloromethane [23], non-polar solvents such as ether [29] and ethyl acetate [30], polymers such as polyethylene glycol [21] and supercritical carbon dioxide (scCO₂) [31] that also form immiscible phases with polar ILs can be used to separate or purify IL solutions. Furthermore, concentrated salts [32] can induce phase separation in aqueous IL solutions, but may not be selective enough for many applications. However, depending on the type and the concentration of solutes remaining after the ILs application, the recovery methods can present some barriers, such as high complexity, demand for large volume of solvent, limited effectiveness, or even degradation and inactivation of IL. Most studies performed are however still preliminary, and more in-depth knowledge is required.

In this work the aqueous solutions of two ILs, 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-enium acetate, [mTBDH][OAc], and 5-methyl-1,5,7-triaza-bicyclo-[4.3.0]non-6-enium acetate, [mTBNH][OAc], are extensively characterized by measuring densities, viscosities, solvatochromic parameters, water activities, solid liquid-equilibria (SLE) and vapor-liquid equilibria (VLE) for these mixtures. Moreover, the recovery of the ILs by liquid-liquid extraction with hydrophobic solvents is investigated. The IL separation is assessed by

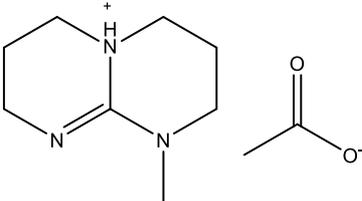
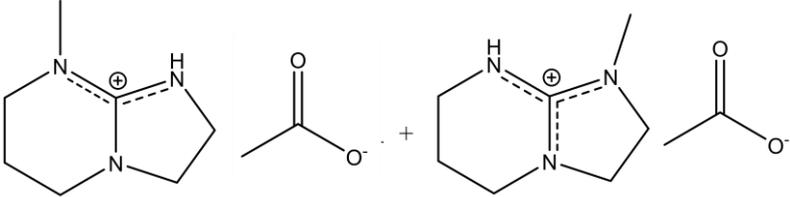
investigating a range of thermodynamic properties of the binary system of IL + water.

2. Experimental

2.1. Chemicals

Table 1 summarizes the information and chemical structures of [mTBDH][OAc] and [mTBNH][OAc]. Superbases-based ILs were dried under vacuum (0.1 Pa and 298.15 K) for at least 72 h. Their water content was measured using a Metrohm 831 Karl-Fischer coulometer, with the analyte Hydranal®. Coulomat AG from Riedel-de Haën. The ultrapure water used in binary mixtures was double-distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus.

Table 1. Properties and chemical structures of [mTBDH][OAc] and [mTBNH][OAc] superbases-based ILs.

Compound	Chemical Structure
7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-enium acetate, [mTBDH][OAc] <i>MM</i> = 213.28 g/mol <i>w</i> t% > 99 ^a <i>w</i> =0.5% ^b Synthesized	
5-Methyl-1,5,7-triaza-bicyclo-[4.3.0]non-6-enium acetate, [mTBNH][OAc] <i>MM</i> = 199.13 g/mol <i>w</i> t% > 97 ^a <i>w</i> =0.5% ^b Synthesized	

^aPurity determined by NMR. ^bWater content measured by Karl-Fischer titration.

2.2. Ionic liquids synthesis

Ionic liquids were synthesized at the University of Helsinki by equimolar mixture (1:1) of acetic acid in the respective superbase (mTBD-H or mTBN-H). To avoid IL crystallization during solvent synthesis, the IL preparation was

carried out in a temperature-controlled glass reactor (80 °C) under continuous agitation for 1 h. The addition of acid was controlled to avoid excessive heating [15]. It is important to point out that the mTBN-H superbase is structurally similar to mTBD, but the first contains five- and six-membered rings . Fig. 1. Therefore, the resulting [mTBNH][OAc] exists as a double-structured IL including two isomers, as shown in Table 1. The mTBN is available in a stoichiometric ratio of 4:3 (a:b) as well as the isomer a:isomer b proportion of the resulting IL. To confirm the purity and the success of ILs synthesis, their structures were analyzed by ¹H-NMR and ¹³C-NMR techniques (Figs. S1-S4).

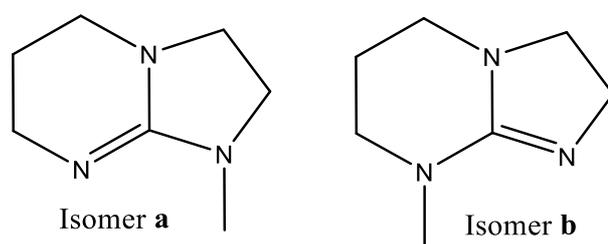


Fig. 1. Structure of mTBN superbase. mTBN is a mixture of two isomers (isomer a and isomer b) which differ in the location of the double bond, and consequently the methyl group position.

2.3. Experimental Procedure

The following sections describe in-depth the experimental methodologies used in this work. Binary mixtures between ILs and water were prepared in different proportions covering the full compositions range (at mole fraction intervals of 0.1) by weighting the proper amounts of each pure substance. ILs were weighted inside a dry-argon glovebox using an analytical balance (model ALS 220-4 N from Kern, with a repeatability of 0.2 mg) with a mole fraction uncertainty of 0.002. Vials were then closed with a septum and posteriorly sealed with an aluminium crimp. Water was weighted using a syringe at room conditions using an analytic balance Mettler Toledo XP205 (repeatability of 0.015 mg). Mixtures were placed under stirring till a homogeneous liquid was formed and stored in a desiccator.

2.3.1. Solid-liquid equilibria (SLE)

The melting temperatures and enthalpies of pure ILs and their mixtures with water were determined through differential scanning calorimetry (DSC) by using a Hitachi DSC7000X working at atmospheric pressure and coupled to a liquid nitrogen cooling system. Samples of approximately 10 mg were weighted in a micro-analytical balance AD6 (PerkinElmer, precision = 0.002 mg) and then carried out as fast as possible to avoid water absorption. Cooling and heating cycles at 5 and 2 K min⁻¹, respectively, were performed. Thermal transitions were taken as the peak temperature. The equipment was previously calibrated with several standards (heptane, octane, decane, 4-nitrotoluene, naphthalene, benzoic acid, diphenylacetic acid, indium, tin, caffeine, lead, zinc, potassium nitrate, water, and anthracene) presenting weight fraction purities higher than 99%.

2.3.2. Vapor-liquid equilibria (VLE)

The vapor-liquid equilibrium data of mixtures of water and ILs were determined at 0.005, 0.05 and 0.1 MPa using an internal isobaric microebulliometer. The experimental apparatus was described and optimized in previous publications [33,34]. Briefly, the equipment consists of 3 sections, a glass camera (with a volume of 8 ml) coupled to an aluminum block with temperature and agitation control, a temperature-controlled glass condenser (thermostatic bath), and a liquid injection system. A type K thermocouple (calibrated by comparison with a NIST-certified Fluke Calibration 1521 thermometer) was used to measure the temperature of the liquid phase. The internal system pressure was kept constant using a Büchi vacuum pump (model v-700) and the pressure was monitored by the Büchi pressure controller (model 728A). During the tests, the equilibrium of the system was considered achieved when the temperature remained constant (deviation less than 0.05 K min⁻¹). The composition of the liquid phase was determined at 323 K using an Anton Paar Abbemat 5010 refractometer, with an uncertainty of 2×10^{-5} nD. A calibration curve was previously performed using standards with different compositions (uncertainty of 1×10^{-4} g).

2.3.3. Water activity

The water activity (a_w) of aqueous mixtures of ILs was measured using a water activity instrument (Novasina hygrometer LabMaster-aw) at 298.15 K. The methodology used was previously described and optimized [35]. The instrument was initially calibrated with seven standard solutions of NaBr (a_w ranging from 0.5916 to 0.8888). NaBr was previously dried during 48 hours in an oven at 105 °C. Subsequently, the mixture of ILs and water (approximately 2-3 ml) was placed in the air-tight equilibrium chamber and the a_w measured. Some measurements were outside the calibration range performed using NaBr, in these cases, the points were extrapolated. To check the accuracy, the measurement of ILs samples were interspersed with NaBr measurements.

2.3.4. Kamlet-Taft solvatochromic parameters

The Kamlet-Taft (KT) solvatochromic parameters π^* , α , and β were measured for the mixtures of ILs and water at 298 K. The parameters π^* and α were determined (in triplicate) through the solvatochromic probes N,N-diethyl-4-nitroaniline and 4-nitroaniline, respectively, by a colorimetric method using a BioTeck Synergy HT UV microplate reader. β was determined using an alternative probe, pyridine-N-oxide, through NMR spectroscopic data (Bruker Avance 300 at 75 MHz) [36]. The equations used to calculate the parameters π^* , α , and β are available in the supplementary material.

2.3.5. Viscosities and density measurements

Viscosities and densities of aqueous solutions of ILs and neat ILs were measured at atmospheric pressure over a temperature range of 293.15 to 363.15 K. Measurements were performed on a SVM 3001 Anton Paar viscometer-densimeter (temperature uncertainty: ± 0.03 K; absolute density uncertainty: 1×10^{-4} g cm⁻³, relative viscosity uncertainty: 0.35%).

2.3.6. Ionic liquid recovery from aqueous solution

Ionic liquids aqueous solutions were prepared by directly dissolving the ILs in ultra-pure water at a concentration of 20 wt% and posteriorly mixing it with

the hydrophobic extractant in an organic to aqueous phase volume ratio of 1:1. Extractions were performed in Eppendorf encapsulated flasks by stirring them vigorously in a Thermomixer Comfort (2 h, 1400 rpm) or in vortex (90 s), respectively. Encapsulated flasks were left to equilibrate during 12h at room conditions. Phase separation occurred quickly after cessation of the stirring process. The aqueous phase was posteriorly collected with a syringe and analysed using a BioTeck Synergy HT microplate reader at 298 nm and at room temperature. The extraction efficiency (*EE*) for a given ionic liquid (IL) was calculated by the following equation:

$$\frac{C_{aq} - C_{aq}'}{C_{aq}} \times 100 \quad (2)$$

where the subscript *aq* denotes the aqueous phase and *i* and *f* the time frame (*i* . before extraction and *f* . after extraction). The phase volume ratio was considered practically unchanged due to the negligible mutual solubilities among the aqueous and organic phases.

3. Results and Discussion

3.1. Density and Viscosities

Density and viscosity are fundamental physical properties of a solvent and are extremely important in the design, operation, and optimization of any application, since they may be correlated with the solvent fluidity and mass transfer [37]. In general, a useful solvent should have low viscosity for better mass transfer and a density sufficiently different from water for good phase separation. Therefore, in this study, the viscosity and density of ILs and their aqueous solutions were determined to further characterize the investigated mixtures (Fig. 2 and Fig. 3 and Tables S1, and S2). Density and viscosity data were not determined for mixtures of [mTBDH][OAc] with low water content ($x_{\text{water}} < 0.45$), due to the high melting temperature of these mixtures.

Results show that both pure ILs and their aqueous solutions have higher viscosity and density than water and, as expected, density and viscosity

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Synopsis. The physicochemical characterization of mixtures of ILs and water is herein demonstrated to highlight the challenges in recovering hydrophilic ILs from aqueous solutions.