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

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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, Kamlet–Taft solvatochromic parameters, densities, and viscosities. An experimental screening of 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 Hydralan®–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.

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

<sup>a</sup>Purity determined by NMR. <sup>b</sup>Water 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 sealed in hermetic aluminum crucibles (0.3 MPa, 7.5 μL). This procedure was 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 $2 \times 10^{-5}$ nD. A calibration curve was previously performed using standards with different compositions (uncertainty of $1 \times 10^{-4}$ g).
2.3.3. Water activity

The water activity ($a_w$) of aqueous mixtures of ILs was measured using a water activity instrument (Novasinhaygrometer 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 $\alpha$, $\beta$ and $\pi^*$, were measured for the mixtures of ILs and water at 298 K. The parameters $\pi^*$ and $\beta$ 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. $\alpha$ parameter 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 $\alpha$, $\beta$ and $\pi^*$ 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: $1 \times 10^{-4}$ 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’s or encapsulated flasks by stirring them vigorously in a Thermomixer Comfort (2 h, 1400 rpm) or in vortex (90 s), respectively. Eppendorf’s were centrifuged during 15 minutes at 13300 rpm and 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:

\[
\%EE = \left( \frac{[IL]_{aq,f} - [IL]_{aq,i}}{[IL]_{aq,i}} \right) \times 100
\]

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 \([\text{mTBDOAc}]\) 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
decrease with increasing temperature. This behaviour is related to thermal expansion; the fluid density decreases and the intermolecular interactions become weaker due to the increase in the mutual distances between the molecules and, therefore, the viscosity also decreases [38]. It is observed that the density of aqueous mixtures of [mTBNH][OAc] exhibits a maximum, with a value $1.1681 \text{ g.cm}^{-3}$ ($x_{water} \sim 0.5$) at 283.15 K. At this composition, around 1:1 molar ratio, a strong interaction between the molecules of water and [mTBNH][OAc] may be leading to the formation of a water:[mTBNH][OAc] complex. Similar behavior was observed for aqueous mixtures of [EMIM][OAc] [39]. Above this maximum, the addition of water leads to a decrease in the mixture density. However, as can be seen in Fig. 2, this behavior is not symmetric. Due to the difference in densities of the two compounds the decrease in density is more significant on the water-rich side.

**Fig. 2.** Density of mixtures of [mTBDH][OAc] (left) or [mTBNH][OAc] (right) and water as a function of water content at (●) 293.15 K, (●) 313.15 K, (●) 333.15 K, (●) 353.15 K, (●) 373.15 K. Dashed lines are visual guides.
Fig. 3. Viscosity of [mTBDH][OAc] (left) or [mTBNH][OAc] (right) and water as a function of water content at (●) 293.15 K, (●) 303.15 K, (●) 313.15 K, (●) 323.15 K, (●) 333.15 K. Dashed lines are visual guides.

The excess molar volumes ($V^E$) for the studied binary mixtures were calculated from experimental density are depicted in Fig. 4 and Table S3. It was observed that all tested mixtures have $V^E$ values less than zero, that is, negative deviations from ideality across the entire composition range. The high negative deviations from ideality observed for the studied systems and the symmetry of the curves support the idea of a 1:1 water:[mTBNH][OAc] complex formation. For the mixtures containing [mTBNH][OAc] and [mTBNH][OAc], it is observed that the change in the minimum $V^E$ value along the temperature range studied is not significant.

Fig. 4. Experimental excess molar volume, $V^E$, vs. water mole fraction, $x_{\text{water}}$, for the [mTBDH][OAc] + water and [mTBNH][OAc] + water binary mixtures at different temperatures: (▲) 293.15 K; (■) 313.15 K; (♦) 333.15 K; (⬤) 353.15 K; (⬤) 363.15 K; (♦) 373.15 K.
Regarding viscosity, the system [mTBNH][OAc] + water exhibits an atypical behaviour, displaying a maximum value of viscosity of 301.52 mPa.s ($x_{\text{water}} = 0.34$) at 293.15 K (Fig. 3). It was expected that with increasing water content, the ion-ion interaction would be lower due to the solvation of the ions, leading to greater mobility of the ion, which would lead to a decrease in the overall viscosity of the solution. However, for the studied system, there is probably the formation of an arrangement that favors the interaction between molecules, restricting mobility and resulting in increased viscosity.

Density and viscosity data obtained for the mixtures of [mTBNH][OAc] and water were compared with data reported in literature [40] – Fig. S5. Small deviations are observed, being those more pronounced in viscosity. These may be related to the mixture’s preparation, ILs purity, or equipment used. Nevertheless, the trend obtained is in good agreement between the two sets of data.

3.2. Kamlet–Taft solvatochromic parameters

The Kamlet-Taft (KT) solvatochromic parameters are usually determined to better understand the potential of solvents to dissolve cellulose [41]. These parameters provide important information about the ability of a compound or mixture to behave as a hydrogen bond donor ($\alpha$), hydrogen bond acceptor ($\beta$) and their polarizability/dipolarity ($\pi^*$), thus providing important information on the nature of the solvent/mixture.

In this work, the KT solvatochromic parameters of aqueous solutions of ILs were evaluated. Experimental data are shown in Fig. 5 and Table S4. Results show a slight, and expectable, increase in the $\pi^*$ value with increasing water concentration in both systems. Moreover, by increasing the water concentration, a significant increase in the value of $\alpha$ is observed since mixtures with higher water concentrations have a greater capacity to act as hydrogen bond donors [42]. Regarding $\beta$, it decreases with increasing water concentration. The strong hydrogen acidity of water in IL can induce IL anion solvation [43], thus lowering its basicity and causing IL to exit the previously defined dissolution window [44]. For [mTBDH][OAc] + water system with $x_{\text{water}} <$
the KT solvatochromic parameters were not measured due to the high melting point of the pure IL and mixtures.

Results here obtained are in agreement with previous reports demonstrating the negative effect of water on the ability of guanidine-based ILs to dissolve cellulose [14]. Since the addition of water results in anion rehydration causing a decrease in β, which correlates with decreased cellulose solvation in solution and its possible precipitation [44]. Hauru et al. [44] adopted the net basicity (β - α) as a function of β, as a way to classify ILs. Authors showed that a good cellulose dissolution window is in the range of 0.8 < β < 1.2 and 0.35 < β - α < 0.9, meaning that the addition of water alters the net basicity of ILs, making these solutions unable to dissolve cellulose. For the studied mixtures, values of β and β - α (Table S4) were observed within the ideal range for samples with a water concentration lower than x = 0.6. For water concentrations above 0.6 the values of β and β - α are out of the range indicating a low probability of cellulose dissolution.

Fig. 5. Kamlet-Taft solvatochromic parameters: (▲) β, (♦) π* and (●) α of mixtures of [mTBDH][OAc] and [mTBNH][OAc] with water at 298.15 K and as a function of the water molar fraction.

3.3. Solid-liquid phase diagrams

The separation and purification of a solvent is a relevant issue in chemical processes. The use of crystallization allows to recover compounds in
solid form that can be recycled or treated in some other way without an intermediate step of solvent removal, being considered a clean technology. In this sense, the solid-liquid equilibrium of the mixtures of the ionic liquids with water was studied to evaluate the possibility to separate the IL from water by crystallization.

The solid-liquid phase diagram of binary [mTBDH][OAc] + water is depicted in Fig. 6 along with the ideal solubility curves. The detailed experimental data are listed in Table S5 of Supporting Information. Experimental melting temperatures and enthalpies of pure ILs and their mixtures with water were determined using differential scanning calorimetry. For pure [mTBDH][OAc], a melting temperature of 348.9 ± 0.7 K and an enthalpy of melting of 19.5 ± 4.5 kJ.mol⁻¹ was obtained, while for [mTBNH][OAc] the values were 287.5 ±1.8 K and 5.9 ± 0.9 kJ.mol⁻¹, respectively. Given the low melting point of [mTBNH][OAc] the phase diagram was not further explored (Fig. S6).

As can be seen in Fig. 6, the melting temperature was not determined for every molar fraction, due to crystallization difficulties of the liquid mixtures. In the phase diagram, a decrease in the melting point value is observed with the increase of water concentration to around \( x_{\text{water}} = 0.8 \). Additionally, data obtained show an ideal behavior in the IL-rich side \( (x_{\text{water}} < 0.4) \).

The experimental values determined in this study, particularly the melting temperature of [mTBDH][OAc], are in good agreement with the data previously reported in the literature (353.2 K) [12]. It is important to note that for the same anion, the size, charge and charge distribution of the cation are considered to be the main factors influencing the melting point of ILs [45,46]. As expected, [mTBDH][OAc] has a higher melting temperature than [mTBNH][OAc], which must be related to the mixture of the two isomers that constitute the [mTBNH][OAc]. The melting point of the mixture of isomers tends to be lower than the pure isomers, due to symmetry breaking of possible crystals. Symmetry is known to have an important effect on crystal packing efficiency, since a symmetric ion allows for better crystal packing and stronger ionic interactions, increasing the melting point [47].
The COSMO-RS was used to predict the solid-liquid equilibrium of IL+water (Fig. 6 and Fig. S6). As can be seen, the prediction of COSMO-RS can described the IL-rich mixtures significatively well, and suggests that water presents a strong negative deviation to ideality [48].

**Fig. 6.** Solid–liquid phase diagrams for binary mixtures composed of [mTBDH][OAc] + water. Dashed lines represent ideal solubility curves and solid lines represent the COSMO-RS model prediction.

For the studied systems, it was observed a difficulty of crystallization of mixtures with a large amount of water ($x_{\text{water}} > 0.45$). An induction crystallization process, more specifically crystal seeding, a process of adding homogeneous or heterogeneous crystals to a crystallization solution to nucleate more crystals, may be a possible alternative [49].

3.4. Vapor-liquid equilibria (VLE)

Evaporation is one of the most common ways to separate/recover solvents from mixtures. The literature reports a considerable number of studies on recoveries of ILs by evaporation [11,19]. However, the thermal exposure of an IL during the evaporation process can result in thermal decomposition and the formation of undesirable side products [50]. Thereby, the vapor-liquid equilibria of the two ILs with water were studied to explore the possibility of using low-pressure evaporation to separate the IL from water. The isobaric VLE of the binary systems [mTBDH][OAc] or [mTBNH][OAc] with water were measured at 0.100, 0.050, and 0.005 MPa and are depicted in Fig. 7 and
Tables S6 and S7. As expected, the boiling temperatures increase with pressure. For [mTBNH][OAc] + water for example, at $x_{\text{water}} = 0.82$, decreasing the pressure from 0.100 MPa to 0.0500 MPa decreases the boiling temperature by approximately 18 K. The use of vacuum conditions (0.005 MPa) allowed to reduce the equilibrium temperature by approximately 70 K in the entire range of composition studied. These conditions allow not only, because of the lower temperature, to avoid the degradation of IL [50], but also to reduce costs associated with energy consumptions in separation processes. For IL mole fractions higher than 0.6 the low amount of water at the liquid phase leads to unstable experimental conditions hampering the correct description of the complete phase diagram.

The VLE phase diagram was predicted by using the COSMO-RS model. As can be seen in Figure 7, this predictive model describes the experimental data rather well, showing better accuracy at lower pressures (0.005 MPa). Nonetheless, the good extrapolative ability of COSMO-RS allows to draw conclusions about the behavior of the system in the whole concentration range and different pressures.

Regarding the effect of water concentration in the mixture, for both IL ([mTBDH][OAc] and [mTBNH][OAc]), the measured boiling temperature decreases with increasing water concentration. This was expected since it is known that the anion plays a key role in the interaction of ILs with water [51,52]. The IL-water strong interactions lead to the retention of water molecules in the liquid phase, making difficult their displacement to the vapor phase [53]. Therefore, the mixtures boiling temperatures increase with the IL mole fraction. In the water-rich region ($x_{\text{water}} = 0.8 – 1.0$), there is only a small increase of the boiling temperature as IL concentration increases. In contrast, in the IL-rich phase, a sharp increase of the system’s temperature towards the boiling temperature of the pure ILs can be observed in the COSMO-RS prediction. This same behavior has been reported in the literature for [mTBDH][OAc] [54].

Both systems under study show negative deviation from ideality, that is, water activity coefficients smaller than unity resulting from stronger interactions between IL-water molecules than those found on water-water interactions [33].
This corroborates the data herein obtained, demonstrating that the ILs studied have a high affinity with water.

By comparing the activity coefficients at different pressures studied (0.100, 0.050, and 0.005 MPa) an overlapping of the activity coefficient values with a small deviation in the activity coefficient for the pressure of 0.005 MPa in the region with the least amount of water ($x_{\text{water}} < 0.6$) is observed.

**Fig. 7.** Isobaric vapor liquid equilibrium and activity coefficients of [mTBDH][OAc] + water and [mTBNH][OAc] + water systems at (♦) 0.100, (▲) 0.050 and (●) 0.005 Mpa. Solid lines represent the COSMO-RS model prediction at (▬) 0.1000, (▬) 0.0500, (▬) 0.0250, (▬) 0.0100, (▬) 0.0050, (▬) 0.0025, (▬) 0.0010 Mpa.

3.5. Water activity

The measured water activities and estimated water activity coefficients for mixtures of ILs and water are displayed in Fig. 8 and Table S9. These
provide isothermal (rather than the isobaric as discussed above) information about the VLE of ILs and water. Both systems studied have water activity coefficients at 298 K below 1, supporting the favorable interactions between ILs and water discussed above. At low water concentrations ($x_{\text{water}} < 0.6$) the interactions between IL and water are very strong, resulting in very low water activities. The water activity increases in general with the water concentration due to the increased probability of interactions between water molecules [35]. However, it is possible to observe an increase in the water activity coefficient for the [mTBNH][OAc] + water mixture with a decrease in the water content in the region with a concentration below $x_{\text{water}} = 0.4$. This behavior occurs in the same region where it was observed an anomalous behavior of viscosity (Fig. 3). Therefore, it may be related to the interactions of [mTBNH][OAc] and water molecules at these concentrations, since the activity coefficient has the lowest value at the concentration at which a maximum on the viscosity is observed, that is, a stronger interaction between these molecules. The COSMO-RS model was able to predict well the behavior of the water activity coefficient for a temperature of 298.15 K, however it not able to describe the atypical behavior in the IL-rich region ($x_{\text{water}} < 0.4$).

Comparing the activity coefficients of water obtained in an isothermal system and those obtained in an isobaric system (Fig. S7) it is possible to observe the temperature influence since the isothermal water activity coefficients were obtained at 298.15 K and the isobaric are obtained at a range of 300-420 K. These results show that at low temperature the interactions are stronger (values of coefficients of lower water activity) as might be expected from a system dominated by hydrogen bonding [55].

Therefore, with the VLE and water activity data obtained, it is possible to state that the pressure reduction implies a decrease in the boiling temperature, which consequently implies an increase in the interactions between IL molecules and water. Therefore, the approach of reducing the pressure to minimize energy costs to reduce the boiling temperature must be used to a certain point where there is not a high increase in molecules interactions, to ensure energy minimization.
Fig. 8. Water activity (left) and water activity coefficient (right) of aqueous mixtures of (▲) [mTBDH][OAc] or (●) [mTBNH][OAc] as a function of water molar concentration. Solid lines represent the COSMO-RS model prediction for (—) [mTBDH][OAc] and (—is) [mTBNH][OAc] at 298.15 K.

3.6. Extraction efficiency

Liquid-liquid extraction is a method used to separate a component of a mixture based on its different solubilities in two immiscible liquids, usually water and an organic solvent. It is often applied to extract thermally sensitive components [56]. Therefore, liquid-liquid extraction is based on the non-miscibility of ILs with solutions. For example, hydrophilic ILs can be extracted by water from hydrophobic systems [57]. In this sense, the recovery of [mTBDH][OAc] and [mTBNH][OAc] by liquid-liquid extraction with hydrophobic solvents are investigated (Table S10). The selection was based on the solvent properties, namely the enthalpy of vaporization, water solubility, and melting point. Solvents should be liquid at room temperature, non-miscible with water, and volatile.

Among the 17 hydrophobic solvents tested, a maximum extraction efficiency of 70% and 36% for [mTBDH][OAc] and [mTBNH][OAc], respectively, was achieved using dichloromethane (Fig. 9). Petroleum ether, cyclohexane, hexane, ethyl decanoate, MTBE, xylene, p-cymene, and 2-undecanone were not able to extract the studied ILs from water. This low extraction can be associated with the poor interaction (solubility) of these polar and strongly
hydrophilic ILs with these apolar solvents. Better results are obtained with hydrophobic alcohols and with dichloromethane and 1,2-dichloroethane.

To try to develop tools for a selection of solvents for extraction, the solubility between the studied ILs and solvents was studied using COSMO-RS (Fig. S8) to estimate the infinite dilution activity coefficient ($\ln(\gamma^\infty)$) of ILs in the different solvents. A lower value of $\ln(\gamma^\infty)$ indicates a better solvent dissolution capacity. As shown in Fig. 9, the solvents located farthest to the right with a value of $\ln(\gamma^\infty)$ less than 10, are the solvents with the greatest capacity to dissolve and consequently extract the ILs. This shows that it is possible to identify the best solvents for extraction of ILs using COSMO-RS.

Other parameters that were studied to evaluate ILs potential to select solvents were the dielectric constant ($k$), the dipole moment ($\mu$) and Kamlet-Taft solvatochromic parameters (Table S10 and Fig S9). The dielectric constant of a solvent can be considered as its ability to reduce the effective internal charge of the solute. Therefore, the dielectric constant of a solvent can be used as a parameter of the solvent's ability to dissolve ionic compounds, such as ILs [58]. It is observed that $k > 4$ resulted in higher selection efficiency (Fig.9), but there are clear deviations indicating that the dielectric constant has an effect but alone is not able to describe the behavior of solvents. Therefore, the combination of parameters must be used to assess the ability to extract solvents to be used in the separation of IL. Based on the results obtained in this study, solvents with higher IL extraction capacity should have high dielectric constant ($k > 4$) and high dipole moments.
Fig. 9. Extraction efficiency (EE%) of (■) [mTBDH][OAc] and (■) [mTBNH][OAc] (20 wt%) in hydrophobic solvents versus activity coefficients at infinite dilution ($\gamma_\infty$) of (●) [mTBDH][OAc] and (♦) [mTBNH][OAc] and (▲) dielectric constant ($k$) of solvents.

To evaluate the possibility of the use of dichloromethane, the solvent that provided the maximum extraction efficiency, the stability and integrity of the IL after extraction was verified. The ILs structure after extraction with dichloromethane in both aqueous and organic phases was investigated by NMR– Fig. S10 to S13. Results show a different behaviour of the NMR spectra (peaks) in the organic-rich phase. To further investigate this, the $^1$H and $^{13}$C-NMR spectra of IL + dichloromethane with deuterated water ($D_2O$) placed in a coaxial insert were analysed – Fig. S14 to S17. Results revealed that dichloromethane reacts with the IL anion, acetate, leading to the production of methylene diacetate and/or chloromethyl acetate. This reaction was previously reported by Cohen et al [59] that found that dichloromethane mixed with 1-ethyl-3-methylimidazolium acetate leads to acetylation by nucleophilic displacement of the acetate anion with a chloride ion. It can, thus, be concluded that dichloromethane reacts with [mTBDH][OAc] or [mTBNH][OAc] leading to
the production of methylene diacetate and/or chloromethyl acetate. The formation of these new compounds can be an advantage, when it is intended, for example, to use this system to dissolve cellulose and produce cellulose acetate [60]. However, in the case of IL recovery, this is undesirable, as there is the consumption of dichloromethane and the loss of the structure of IL, our target product for recovery. Therefore, and due to its reactivity with IL, the use of dichloromethane should be avoided in this process and alternative solvents, such as butanol, that do not react with IL during the extraction process should be considered.

4. Conclusions

The present work shows the physical-chemical characterization of the binary systems water + [mTBDH][OAc] or [mTBNH][OAc]. The densities and viscosities of the aqueous mixtures of ILs were measured and maxima on these properties were identified suggesting the formation of complexes or special organization of the interactions at specific stoichiometric proportions, in all cases revealing a strong interaction between the ILs and water.

The solid-liquid equilibrium, including the melting properties of pure ILs, are reported. The higher melting temperature of [mTBDH][OAc] compared with [mTBNH][OAc] may be partly explained by the fact that the second is a mixture of the two isomers. The vapor-liquid equilibrium and the water activity were also measured under different conditions. In both systems investigated, the boiling temperature of water decreases with increasing water concentration, and negative deviations from ideality are observed, in agreement with the observed maxima for the densities and viscosities. The water activity coefficients show favourable interactions between ILs and water.

The liquid-liquid extraction of superbase ILs with hydrophobic solvents was investigated. A maximum extraction efficiency of 70% and 37% was achieved for [mTBDH][OAc] using dichloromethane and butanol as extractants, respectively. However, it was found that dichloromethane reacts with the IL anion, acetate, leading to the production of methylene diacetate and/or chloromethyl acetate. Therefore, due to its reactivity with IL, the use of
chlorinated solvents should be avoided when the production of methylene diacetate is not intended. The results analysis show that is possible to correlate the extraction efficiency of IL with the dielectric constant and infinite dilution activity coefficient of solvents. Therefore, these parameters can be used as guides for the selection of more efficient solvents for IL extraction.

The results herein presented highlight the challenges in recovering hydrophilic ILs from aqueous solutions and present a set of physicochemical properties that can be used to design the best process to recover and recycle them.

Credit Author Statement

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Notes

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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.