

# Recovery of superbase ionic liquid using aqueous two-phase systems

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## ABSTRACT

Aqueous two-phase systems (ATPS) have been widely used for the purification and separation of biomolecules. However, recent studies have shown that ATPS can also be effective in the purification and recovery of other compounds, such as ionic liquids (IL). Here, we investigated the liquid-liquid phase equilibria of ATPS consisting of 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ( $[mTBNH][OAc]$ ) and potassium salts ( $K_2CO_3$  and  $K_3PO_4$ ) at 293.2 K and 323.2 K. Our results indicate that both systems exhibited a high IL partition coefficient ( $k$ ), exceeding 9.5, and achieved a 99.5% recovery of ionic liquid. Moreover, we found that the presence of potassium salt in the ionic liquid-rich phase had a negative impact on the IL cellulose dissolution capability. Therefore, we investigated the removal of potassium salt from the IL and successfully achieved it by using a nanoporous sodium zirconium cyclosilicate (ZS-9 or AV-13). Overall, our study suggests that ATPS can be a promising technique for the purification and recovery of ionic liquids, with potential applications in various industries.

## 1. Introduction

In recent years, the growing global population and subsequent increase in the consumption of fibre-based products, ranging from textile manufacturing to automobile production, has led to a surge in demand for both natural and synthetic fibres [1,2]. The global fibre production increased again to a record 113 million tonnes in 2021 and is expected to grow to 149 million tonnes by 2030 [3]. The rising concern over the environmental impact of synthetic polymers utilized in fibre production has resulted in a demand for more sustainable alternatives. This has led to an increased demand for cellulose fibres as a more environmentally friendly option [4]. Cellulose fibres are produced by dissolving cellulose and extruding it into fibre form. These fibres are renowned for their strength, durability, and other desirable properties, making them a popular choice for various applications. Rayon, modal, and lyocell are some examples of cellulose fibres [5,6]. Despite their many benefits, the conventional methods used to produce cellulose fibres have significant drawbacks. They involve the use of hazardous solvents that are harmful to both people and the environment.

Several studies have investigated alternative processes and solvents for producing cellulose fibres. One example of such a process is the Ioncell process, which employs an ionic liquid as a solvent to dissolve the cellulose. The dissolved cellulose is then extruded through a spinneret to form the fibres. This process offers a more environmentally

friendly approach to cellulose fibre production [7]. Compared to traditional methods of producing cellulose fibres, the Ioncell process is considered a more sustainable option. This is because it uses a renewable and biodegradable solvent, and generates less waste than other processes [8–10]. However, of the various ILs capable of dissolving cellulose, only a small portion has a high dissolution capacity and acceptable spinning properties. Recently, the superbases IL, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium,  $[mTBDH][OAc]$  and 5-methyl-1,5,7-triaza-bicyclo[4.3.0]enium non-6-acetate,  $[mTBNH][OAc]$ , were identified as solvents with high potential to be applied in the Ioncell process [11,12]. Elsayed et al. [13] demonstrated that  $[mTBDH][OAc]$  has a high water tolerance, being able to dissolve cellulose even at high water concentrations (58 mol%).

In the Ioncell process, after the cellulose is dissolved in the ionic liquid, the fibre is regenerated in a coagulation bath. This step removes the water-soluble ionic liquid, which is then recovered as a diluted aqueous solution ( $w_{IL} \approx 20$  wt%). Recovering and recycling the IL is necessary to reduce operational costs and the environmental impact of the process [14]. This requires concentrating the IL to a minimum concentration of 80 wt%. Because the IL has a negligible vapour pressure the evaporation is conventionally used to separate water from IL [15]. However, this process is highly energy-intensive and may require high temperatures depending on the operating pressure. At such high temperatures, some ionic liquids may undergo degradation, which can be a

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significant drawback of the process.

Processes such as extraction (liquid-liquid, supercritical) [16], membrane separation (nanofiltration, reverse osmosis) [17,18], precipitation, adsorption [19], crystallization [20], electro dialysis [21] have been reported in the literature for the separation of IL from aqueous solutions. Most of these approaches come with some significant drawbacks, such as low selectivity, high solvent consumption, and high energy requirements. However, these drawbacks can be effectively minimized by adopting a more environmentally friendly alternative, such as the use of liquid-liquid extraction based on aqueous two-phase systems (ATPS).

An ATPS is formed by mixing solutions of a polymer and a salt, which can either be a polymer and a salt, two polymers, or two salts [22,23]. Gutowski et al. [24] showed that the addition of inorganic salts to aqueous solutions of ionic liquids (ILs) may also cause liquid-liquid demixing and induce ATPS formation. ATPS is a promising approach for recovering hydrophilic ILs from aqueous solutions since the IL can be concentrated in an IL-rich phase. Several authors investigated the recovery and purification of IL using ATPS [25]. Deng et al. [26] reported a maximum IL recovery of 96.8% in 1-allyl-3-methylimidazolium chloride - [Amim][Cl]/salt systems. The authors also demonstrated that the IL recovery in these systems depends on the salt concentration and its position in the Hofmeister series. Shill et al. [27] used an aqueous inorganic (kosmotropic) salt solution to precipitate the cellulosic components pre-treated with IL and induce the formation of an ATPS. The formed ATPS allowed the concentration of the diluted IL (1-ethyl-3-methylimidazolium acetate - [C<sub>2</sub>C<sub>1</sub>im][AOc]). The use of K<sub>3</sub>PO<sub>4</sub>-based ATPS has enabled the recovery of more than 95% of the ionic liquid. However, it is worth noting that the repeated reuse of the ionic liquid has been observed to have a negative effect on saccharification yields. In another study, Gao et al. [28] used the same salt, K<sub>3</sub>PO<sub>4</sub>, to form ATPS and recover imidazolium-based IL after dissolving the biomass with IL/dimethyl sulfoxide. Recovery rates between 54.3–96% were obtained. Other salts, such as aluminium sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) and potassium aluminium sulfate (AlK(SO<sub>4</sub>)<sub>2</sub>), have also been used to recover IL from contaminated aqueous solutions [29]. Multi-step ATPS has been used to recover IL (1-butyl-3-methylimidazolium chloride - [C<sub>4</sub>C<sub>1</sub>im]Cl) of dissolved carbohydrates. The use of an 80% potassium phosphate solution was found to enable the recovery of around 60% of the ionic liquid [30].

The aim of this study is to establish the liquid-liquid phase equilibria of ternary systems made up of water, salts, and superbase ionic liquids, with the goal of enabling the recovery and recycling of the ionic liquids. The potential of potassium salts (K<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub>) and a superbase IL, 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate [mTBNH][OAc], which is considered an excellent candidate for the production of high-performance cellulose fibers, was investigated for the formation of aqueous two-phase systems. Experimental binodal data were collected at 293.15 K and 323.15 K and modelled using the nonrandom-two-liquid (NRTL) model. Contamination of the ionic liquid phase by potassium has been found to have a negative impact on cellulose dissolution. In order to mitigate this issue, the removal of potassium from the IL was explored using different methods, including the use of antisolvents such as ethanol and acetone, as well as the application of a nanoporous sodium zirconium cyclosilicate. This inorganic ion-exchange resin is composed of a framework structure similar to ZS-9 [31] or AV-13 [32] materials. It features pore openings of approximately 3 Å that are surrounded by asymmetrical seven-membered rings.

## 2. Experimental section

### 2.1. Materials

The superbase-based IL, 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate, [mTBNH][OAc] (purity >97%) were synthesized at the University of Helsinki by a stoichiometric mixture (1:1) of acetic acid

and mTBNH. To confirm the success of ILs synthesis, its structures was analysed by <sup>1</sup>H NMR (Figure S1). Potassium carbonate and cellulose (fibres) were obtained from Sigma (Missouri, EUA), and potassium phosphate was obtained from Alfa Aesar (Massachusetts, EUA). All salts were dried in an oven at 377.15 K for 4 h before use. Ultrapure water (Milli-Qplus 185 water purification apparatus) was used in all experiments. The water content of the solutions was determined using a Metrohm 831 Karl-Fischer coulometer, with the analyte Hydranal-Coulomat AG from Riedel-de Haën. The purity, supplier, and CAS number (CAS) of the chemicals are listed in Table 1. ZS-9 or AV-13 was synthesised according to the methods described in [33] or in [32] (followed by acid ion exchange).

### 2.2. Methods

#### 2.2.1. Binodal curves measurements

The cloud point methodology was used to determine the binodal curves experimentally [34,35]. This approach is based on titration of the salt solution in the IL solution, or vice versa, until a cloud point is observed. Water was then added to the system to make it homogeneous, and the procedure was repeated until enough points were obtained for constructing the binodal curve. The amount of water, salt, or IL added to the system was quantified by gravimetric analysis (Mettler Toledo XP205, repeatability of 0.015 mg). The curves were obtained at 298.2 K and 323.2 K, and local atmospheric pressure (102.8 kPa).

#### 2.2.2. Determination of tie-lines

The quantification of phase compositions was based on the method proposed by Merchuk et al. [36] Briefly, this method consists of a least squares regression of the objective function (Eq. S1) using the empirical relationship proposed by Merchuk et al. [36] (Eq. (1))

$$Y = A \exp[(BX^{0.5}) - (CX^3)] \quad (1)$$

Where  $X$  and  $Y$  are the salts and IL weight percentages, respectively, and the constants  $A$ ,  $B$  and  $C$  were obtained by least squares regression of the binodal curve. The composition of the tie lines was determined by applying the lever rule to the relationship between the mass phase composition and the overall system composition. For this, a system of four equations (Eq.(S2-S5)) and four variables ( $Y_T$ ,  $Y_B$ ,  $X_T$ , and  $X_B$ ) was solved applying the generalized reduced gradient (GRG) optimization method [35].

The tie-line length (TLL) is expressed by the difference between the concentration of salt ( $X$ ) and IL ( $Y$ ) in the top ( $T$ ) and bottom ( $B$ ) phases and is defined by (Eq. (2))

$$TLL = \sqrt{(X_T - X_B)^2 + (Y_T - Y_B)^2} \quad (2)$$

in which  $X_T$ ,  $X_B$ ,  $Y_T$ , and  $Y_B$  represent the equilibrium compositions of the salt and IL in the top and bottom phases, respectively.

Another important parameter, the slope of the tie line (STL), was calculated from the ratio of the difference between the concentration of the IL and the salt in the top and bottom phases (Eq. (3))

**Table 1**  
Source and purity of the compounds.

Name	Purity assay(%)	Supplier	CAS
5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc])	>97.0%		
Potassium Carbonate (K <sub>2</sub> CO <sub>3</sub> )	99.0%	Sigma	584-08-7
Potassium phosphate (K <sub>3</sub> PO <sub>4</sub> )	97.0%	Alfa Aesar	7778-77-0
Ethanol	>99.0%	Fisher Scientific	64-17-5
Acetone	>99.0%	Fisher Scientific	67-64-1

$$STL = \frac{(Y_T - Y_B)}{(X_T - X_B)} \quad (3)$$

The partition coefficient ( $k$ ) was determined as the ratio between the IL concentration in the top phase ( $[IL]_T$ ) and the bottom phase ( $[IL]_B$ ) (Eq (4)).

$$k = \frac{[IL]_T}{[IL]_B} \quad (4)$$

The ionic liquid recovery (%  $IL_{Recovery}$ ) of each tie-line was calculated considering the IL equilibrium concentration in the IL and salt-rich phases (Eq. (5))

$$\% IL_{Recovery} = \frac{(m_T \cdot Y_T)}{(m_T \cdot Y_T + m_B \cdot Y_B)} * 100 \quad (5)$$

Where  $m_T$  is the mass of the top phase (IL-rich), and  $m_B$  is the mass of the bottom phase (salt-rich).

### 2.2.3. Cellulose dissolution

The dissolution of cellulose in [mTBNH][OAc] aqueous solution (85 wt%) was examined using optical microscopy [37]. The dissolution of cellulose (5 wt%) was evaluated in aqueous solutions of [mTBNH][OAc] at different concentrations of  $K_2CO_3$  (1, 2, 2.5, 3.5, 4.5, and 5 wt%). The samples were kept under agitation (200 rpm) for 48 h at 80 °C. Afterward, approximately 50 mg suspension was dropped in a glass coverslip and observed on an optical microscope (Leica DM2700M, Germany), and an image (2048 × 1536 pixels) was collected to evaluate the cellulose dissolution.

### 2.2.4. Potassium removal

The removal of  $K^+$  ion from the [mTBNH][OAc]-rich phase was attempted using two methods. The first method consisted of adding ethanol or acetone to precipitate  $K_2CO_3$ . Ethanol or acetone was added in a 1:3 and 1:5 ratio, and the solution was stirred, centrifuged for 10 min at 12,000 rpm, and the liquid phase was separated from the precipitated salt. In the second method, an inorganic ion-exchange resin, sodium chloride stannosilicate AV-13 ( $Na_{2.26}SnSi_3O_9Cl_{0.26}$ ), was used to remove  $K^+$ . Between 100 or 200 mg of resin was added to samples of 500 mg. The samples were kept under gentle agitation 20 rpm (Trayster,

IKA) for 4 h at 298.2 K. The potassium content solution was evaluated via total reflection X-ray fluorescence spectrometry (TXRF S2 Picofox, Bruker) by dissolving the sample in a solution of 0.2 g of Triton® X-100 (1 wt%) and 0.8 g of poly(vinyl alcohol) (1 wt%), spiked with a known concentration of yttrium.

## 3. Results and discussion

### 3.1. Liquid-liquid phase diagrams

The ability of the salts to induce the formation of ATPS from aqueous [mTBNH][OAc] solutions was evaluated by determining the corresponding ternary phase diagrams, amongst the 32 salts tested (Table S1) only  $K_2CO_3$  and  $K_3PO_4$  led to the formation of ATPS with water and [mTBNH][OAc]. This behaviour is attributed to differences in the hydration molar entropy values of the saline ions involved [38,39]. Bivalent cations exhibit a stronger salting-out effect compared to monovalent ions, resulting in a higher tendency to induce the formation of ATPS. As a result, salts like sodium chlorate (NaCl), caesium chloride (CsCl), and potassium chloride (KCl), which are weak salting-out species, have less propensity to form two phases when mixed with an IL aqueous solution. Furthermore, salts containing trivalent anions such as  $PO_4^{3-}$  exhibit a stronger salting-out capacity than those containing divalent anions such as  $CO_3^{2-}$ , which are in turn stronger than those containing monovalent anions such as  $Cl^-$ . Martins et al. [40] reported the physicochemical characterization of aqueous solutions [mTBNH][OAc] that revealed the very strong interactions between the IL and water molecules. These interactions impede the formation of anion-water complexes, which play a crucial role in the creation of ATPS based on ionic liquids. As a result, these findings can help explain the challenges associated with inducing phase separation using this particular IL.

Experimental data of binodal curves at 298.15 K and 323.2 K at atmospheric pressure (102.8 kPa) for the  $K_2CO_3$  + [mTBNH][OAc] +  $H_2O$  and  $K_3PO_4$  + [mTBNH][OAc] +  $H_2O$  systems are shown in Fig. 1 and the respective tie lines are presented in Fig. 2, respectively. The experimental data (Table S2-S5) and the representation of the complete phase diagram of the system composed of  $K_2CO_3$  + [mTBNH][OAc] +  $H_2O$  (Figure S2) are provided in the supplementary material. The values of parameters of the Merchuk equation (Eq. (1)) used to correlate the data are presented in Table S6. To ensure the reliability of the tie-lines

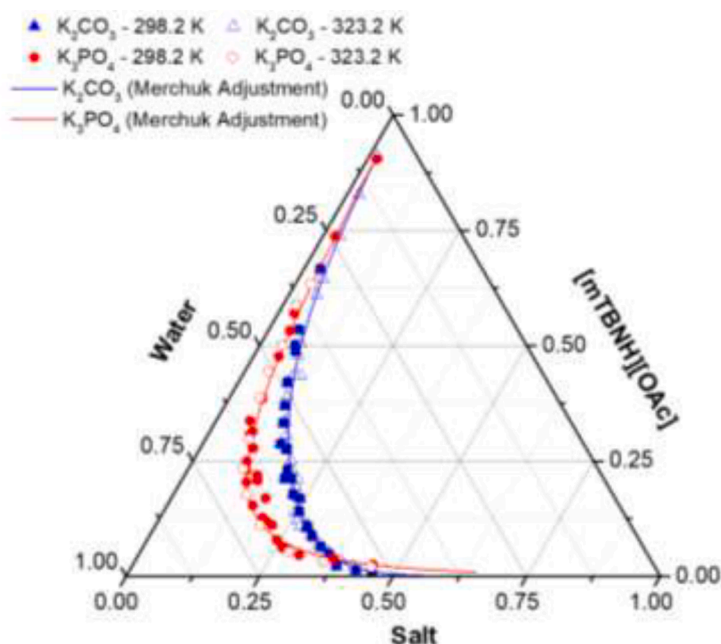


Fig. 1. Binodal curve for the systems:  $K_2CO_3$  + [mTBNH][OAc] +  $H_2O$  and  $K_3PO_4$  + [mTBNH][OAc] +  $H_2O$  at 298.2 and 323.2 K.

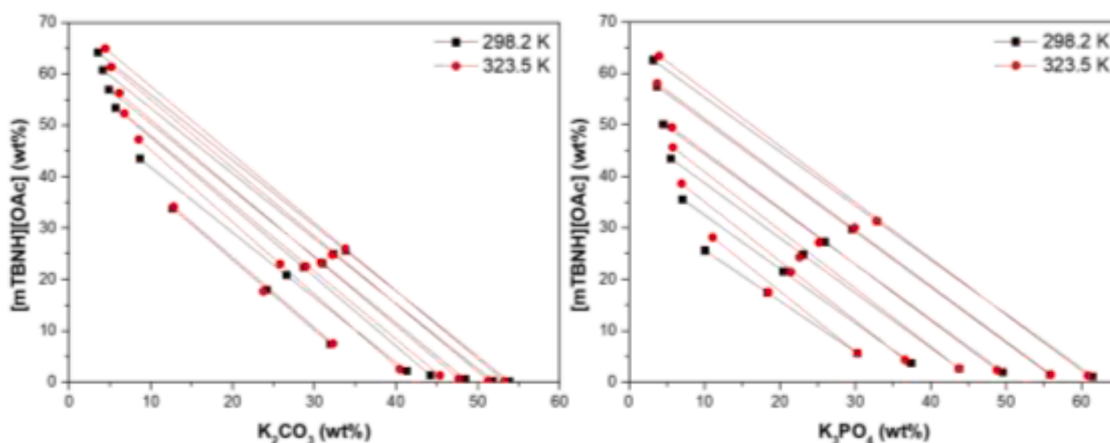


Fig. 2. Tie-lines for the systems:  $K_2CO_3 + [mTBNH][OAc] + H_2O$  and  $K_3PO_4 + [mTBNH][OAc] + H_2O$  at 298.2 and 323.2 K.

Table 2

Equilibrium data for  $K_2CO_3$  (1) +  $[mTBNH][OAc]$  (2) +  $H_2O$  (3) system at 298.2 K and 323.2 K.

TL	Overall		Top phase		Bottom phase		STL	100TLL
	100 $w_1$	100 $w_2$	100 $w_1$	100 $w_2$	100 $w_1$	100 $w_2$		
298.2K								
TL1	24.2	18.0	12.7	33.8	32.0	7.4	-1.4	32.7
TL2	26.6	20.8	8.7	43.5	41.3	2.2	-1.3	52.7
TL3	28.7	22.3	5.7	53.4	44.2	1.3	-1.4	64.7
TL4	31.0	23.2	4.9	57.0	48.4	0.6	-1.3	71.2
TL5	32.4	24.9	4.1	60.8	51.8	0.3	-1.3	77.0
TL6	33.8	25.6	3.5	64.2	53.8	0.2	-1.3	81.4
323.2 K								
TL1	23.7	17.7	12.8	34.2	32.3	7.5	-1.4	33.0
TL2	25.8	23.0	8.5	47.2	40.4	2.5	-1.4	55.0
TL3	29.0	22.6	6.8	52.3	45.4	1.3	-1.3	64.0
TL4	30.8	23.3	6.1	56.3	47.7	0.7	-1.3	69.4
TL5	32.2	24.8	5.2	61.4	51.3	0.3	-1.3	76.5
TL6	33.8	26.0	4.4	65.0	53.2	0.2	-1.3	81.1

Standard uncertainties  $u$  are  $u(w_1) = 0.005$ ,  $u(w_2) = 0.005$ ,  $u(T) = 0.5$  K,  $u(P) = 10$  kPa.

calculated using the Merchuk equation and investigate the possibility of ion exchange in the systems under investigation, we verified the ratio of IL cation to anion in both the top and bottom phases using  $^1H$  NMR (Figure S3). The obtained results demonstrate that the IL cation and anion exist in a molar ratio of 1:1 in both phases, indicating the absence of ion exchange in these systems.

Based on the findings presented in Fig. 1, it can be inferred that the biphasic region of the system involving  $K_3PO_4$  is larger than the corresponding region involving  $K_2CO_3$ , in accord with previous research [39]. These results suggest that  $K_3PO_4$  has a greater propensity to form ATPS with  $[mTBNH][OAc]$  when compared to carbonate, indicating its superior partitioning ability. Therefore, a higher carbonate concentration is required for the same  $[mTBNH][OAc]$  concentration to achieve phase separation. The influence of the salt anion on the phase formation can explain this behaviour. Prior studies have indicated that salt anions with higher molar entropy of hydration values produce a stronger salting-out effect. [39] Given that the molar entropy of hydration of  $PO_4^{3-}$  ( $-421$  J.  $K^{-1}.mol^{-1}$ ) is greater than that of  $CO_3^{2-}$  ( $-245$  J.  $K^{-1}.mol^{-1}$ ), it was anticipated that the anion ( $PO_4$ ) $^{3-}$  would exhibit a stronger salting-out inducing effect [39,41]. Additionally, since these values are much higher than the molar entropy of hydration of  $OAc^-$  ( $-170$  J.  $K^{-1}.mol^{-1}$ ), there is no ion exchange between the salt and the IL.

Six tie-lines were obtained for each ATPS (Table 2 and Table 3). The quantification of phase composition was performed by the method of Merchuk et al. [36]. To ensure the accuracy of the composition quantification, the water concentration was measured in a Metrohm 831 Karl-Fischer coulometer. Table S7 presents a comparison between the water concentration obtained via the Merchuk method and the

Karl-Fischer method. The difference in water concentration between the phases obtained by the two methods is less than 0.5%, indicating that Merchuk's methodology can be reliably applied.

By using the studied salts, it was possible to generate a top phase rich in  $[mTBNH][OAc]$  and a bottom phase enriched with the salt. As shown in Tables 1 and 2 and Fig. 2, an increase in the tie-line length (TLL) leads to the migration of water molecules from the top phase to the bottom phase, resulting in a higher concentration of IL in the top phase. Conversely, the IL concentration decreases in the bottom phase, enabling more effective recovery of the IL from the solution.

At 298.2 K, the maximum  $[mTBNH][OAc]$  concentration attainable for the  $K_2CO_3$  system was 64.2 wt%, while for the  $K_3PO_4$  system a phase with approximately 62.6 wt% of  $[mTBNH][OAc]$  could be obtained. However, the concentration of  $[mTBNH][OAc]$  remaining in the bottom phase was approximately five times lower in the ATPS formed with  $K_2CO_3$  ( $w_{[mTBNH][OAc]} = 0.2$  wt%) than that in a similar tie-line of the ATPS formed with  $K_3PO_4$  ( $w_{[mTBNH][OAc]} = 1.1$  wt%), implying that  $K_2CO_3$  promotes a more effective recovery of  $[mTBNH][OAc]$ .

### 3.2. The effect of temperature

The impact of temperature on the binodal curves and tie-lines of the  $K_2CO_3 + [mTBNH][OAc] + H_2O$  and  $K_3PO_4 + [mTBNH][OAc] + H_2O$  systems was also investigated. An increase from 298.2 K to 323.2 K did not significantly alter the biphasic region of these systems, as temperature did not affect much the interaction forces involved (Fig. 1). Moreover, the tie-line length (TLL) and the slope of tie-line (STL) of these systems exhibited negligible variation with temperature (Fig. 2,

**Table 3**  
Equilibrium data for  $K_3PO_4$  (1) + [mTBNH][OAc] (2) +  $H_2O$  (3) system at 298.2 K and 323.2 K.

TL	Overall		Top phase		Bottom phase		STL	100TLL
	100 $w_1$	100 $w_2$	100 $w_1$	100 $w_2$	100 $w_1$	100 $w_2$		
298.2K								
TL1	18.3	17.4	10.1	25.6	30.3	5.6	-1.0	28.4
TL2	20.4	21.5	7.1	35.5	37.4	3.7	-1.1	43.9
TL3	23.0	24.8	5.5	43.5	43.8	2.6	-1.1	55.9
TL4	25.9	27.2	4.5	50.1	49.5	2.0	-1.1	65.9
TL5	29.5	29.7	3.7	57.5	55.8	1.4	-1.1	76.5
TL6	32.9	31.2	3.2	62.6	61.4	1.1	-1.1	84.7
323.2 K								
TL1	18.4	17.5	11.1	28.1	30.3	5.6	-1.2	29.6
TL2	21.4	21.4	7.0	38.6	36.6	4.3	-1.2	45.3
TL3	22.6	24.3	5.8	45.6	43.7	2.6	-1.1	57.3
TL4	25.2	27.1	5.7	49.5	48.8	2.3	-1.1	63.9
TL5	29.9	30.0	3.7	58.1	55.9	1.4	-1.1	77.0
TL6	32.8	31.3	4.0	63.4	60.8	1.3	-1.1	84.2

Standard uncertainties  $u$  are  $u(w_1) = 0.005$ ,  $u(w_2) = 0.005$ ,  $u(T) = 0.5$  K,  $u(P) = 10$  kPa.

Table 1, and Table 2). This finding is in accord with previous studies, which have demonstrated that the temperature has a minor effect on the binodal curves and tie-lines of ATPS formed by ILs and salts [42,43].

### 3.3. Ionic liquid partition

The liquid-liquid equilibrium data for systems formed by salt and [mTBNH][OAc] allow the evaluation of the partition of [mTBNH][OAc] in the three studied tie-lines. Since ATPS is intended to concentrate and recover the IL, the recovery efficiency must be optimized. The values of the IL partition coefficients ( $k$ ) and IL recovery efficiency (EE%) are presented in Fig. 3.

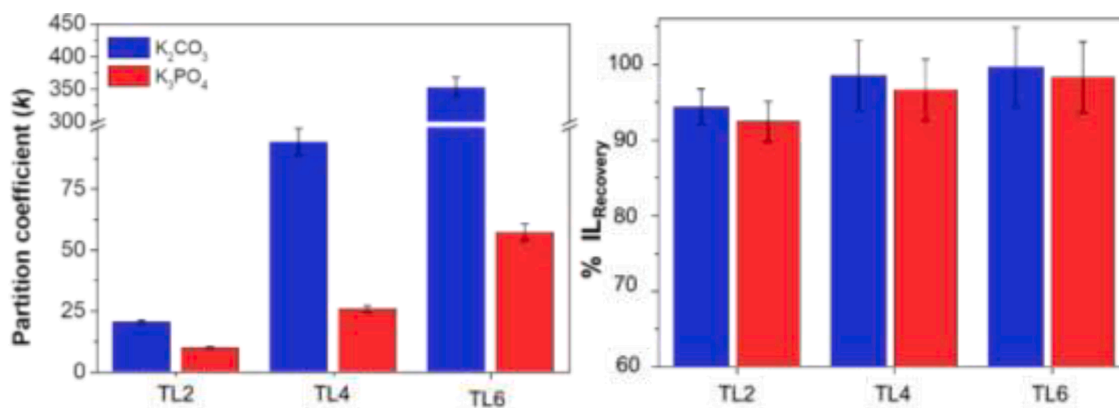
The partition coefficient ( $k$ ) and the IL recovery (%  $IL_{Recovery}$ ) increase with TLL. High values of partition coefficient ( $k > 9.5$ ) and extraction efficiencies of up to 99.5% were achieved. The system with  $K_2CO_3$  exhibited the highest partition coefficient ( $k > 350$ ) for the longest tie-line (TL6), whereas for the system with  $K_3PO_4$ , the maximum partition value was about 6 times smaller ( $k = 56.9$ ), but its impact on the extraction efficiencies was minor. It is important to emphasize that the IL concentration in the top phase is practically the same for both systems. However, the IL concentration in the bottom phase, despite being low (>1.3%), is higher in the  $K_3PO_4$  system, directly influencing the value of the partition coefficient. Moreover, the higher IL concentration in the bottom phase of the  $K_3PO_4$  system results in a greater loss of IL, as the top phase (rich in IL) is the desired phase.

### 3.4. NRTL modelling

The non-random two-liquid model (NRTL) was used to correlate the experimental data in order to enable the computational simulation and optimization of the unit operations involved in the process of separating IL from aqueous solutions using ATPS. Given the promising results of ATPS in this regard and the potential future applications of these systems for the recovery of IL from spinning baths, it is essential to develop a reliable model to predict and optimize their behaviour. NRTL is a commonly used thermodynamic model for correlating and predicting the behaviour of ATPS systems, and its use in this study will provide a foundation for further modelling and optimization of these systems. [44] As the IL has a large molecular mass, it is common to estimate the activity coefficient of component  $i$  in its mass fraction (Eq. S6-S8).

The NRTL model parameters for each system were estimated using the TML-LLE 2.0 program, which utilizes the maximum likelihood principle and the Simplex method. The program compares the experimental data with the model calculations and adjusts the parameters until the best fit is achieved [45,46]. Graphical comparisons between the experimental data and the NRTL model calculations are presented in Fig. 4.

As shown in Fig. 4, the NRTL model is highly effective in describing the experimental data (both binodal and tie-line) for both systems studied. The binary interaction parameters obtained for each system and their corresponding mean square deviations (RMSDs) are listed in Table 4. In all systems the RMSDs were found to be less than 1.22%.



**Fig. 3.** Partition coefficients ( $k$ ) and ionic liquid recovery (%  $IL_{Recovery}$ ) of [mTBNH][OAc] for TL2, TL4 and TL6 of systems composed of  $K_2CO_3$  + [mTBNH][OAc] +  $H_2O$  and  $K_3PO_4$  + [mTBNH][OAc] +  $H_2O$  at 298.15 K and atmospheric pressure.

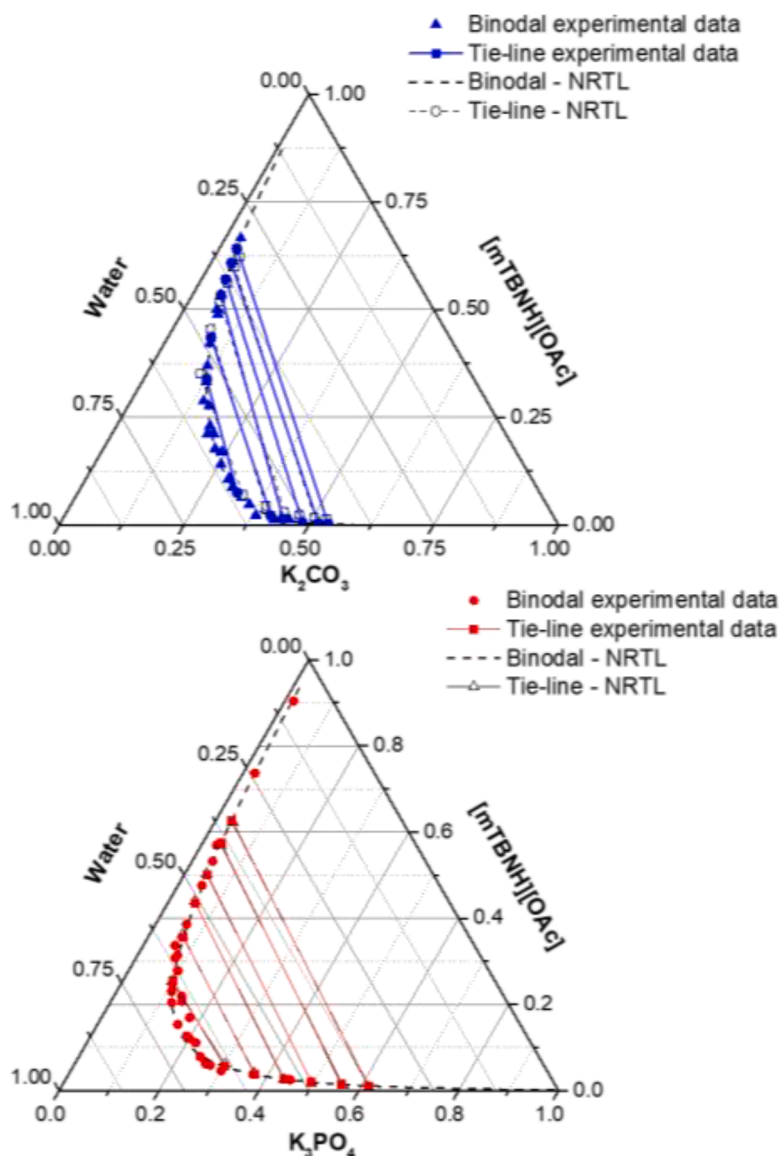


Fig. 4. Experimental and estimated binodal and tie-lines for the systems:  $K_2CO_3 + [mTBNH][OAc] + H_2O$  and  $K_3PO_4 + [mTBNH][OAc] + H_2O$  at 298.2 K.

Table 4

Binary interaction parameters of the NRTL equation and correlation performance for the system used in this work at 298.2 K.

i/j	$A_{ij}$ (K)	$A_{ji}$ (K)	$\alpha_{ij} = \alpha_{ji}$	RMSD <sup>a</sup> (%)
$K_2CO_3 + [mTBNH][OAc] + H_2O$				
$K_2CO_3 - [mTBNH][OAc]$	3454.6	-86.9	0.2000	1.22
$K_2CO_3 - H_2O$	-765.2	2465.2	0.4468	
$[mTBNH][OAc] - H_2O$	-1362.8	2570.7	0.2008	
$K_3PO_4 + [mTBNH][OAc] + H_2O$				
$K_3PO_4 - [mTBNH][OAc]$	2329.6	470.7	0.2000	0.29
$K_3PO_4 - H_2O$	-610.0	1540.8	0.4700	
$[mTBNH][OAc] - H_2O$	-517.8	1416.4	0.4700	

$$^a \text{Root mean square deviation (RMSD)} = 100 \cdot \sqrt{\frac{\sum_i^M \sum_j^N (w_{ij}^{I,exp} - w_{ij}^{I,calc})^2 + (w_{ij}^{II,exp} - w_{ij}^{II,calc})^2}{2MN}}$$

indicating that the NRTL model is capable of accurately representing the phase behaviour of the LLE systems studied. These findings demonstrate the suitability of the NRTL model for modelling and predicting the behaviour of ATPS in the recovery of IL from aqueous solutions.

### 3.5. Potassium removal

ATPS based on potassium salts show a high capacity to concentrate IL in the top phase that is, however, contaminated by potassium. Rabideau et al. [47] found that contaminants such as water and salt ions can reduce the cellulose dissolution ability of IL. To assess the impact of potassium concentration on the dissolution capacity of ionic liquids, cellulose solubility tests were conducted using IL solutions with varying  $K_2CO_3$  concentrations. The researchers chose the carbonate salt due to its high partition coefficient and ability to result in the highest recovery of IL. The microscope images of cellulose dissolved in IL solutions with varying concentrations of  $K_2CO_3$  after 24 h of solubilization are shown in Fig. 5. Cellulose was completely dissolved in the samples with up to 3.5 wt%  $K_2CO_3$ . In the samples with a higher  $K_2CO_3$  concentration the cellulose was not completely dissolved (cellulose fibres are still observed) (see also Figure S4). The result suggests that  $K_2CO_3$  has a detrimental effect on the ability of IL to dissolve cellulose at concentrations above 3.5 wt%. emphasizing the importance of removing potassium from the IL phase to prevent its accumulation and the subsequent decrease in the IL's ability to dissolve cellulose.

Two methods were used to remove residual potassium from the IL

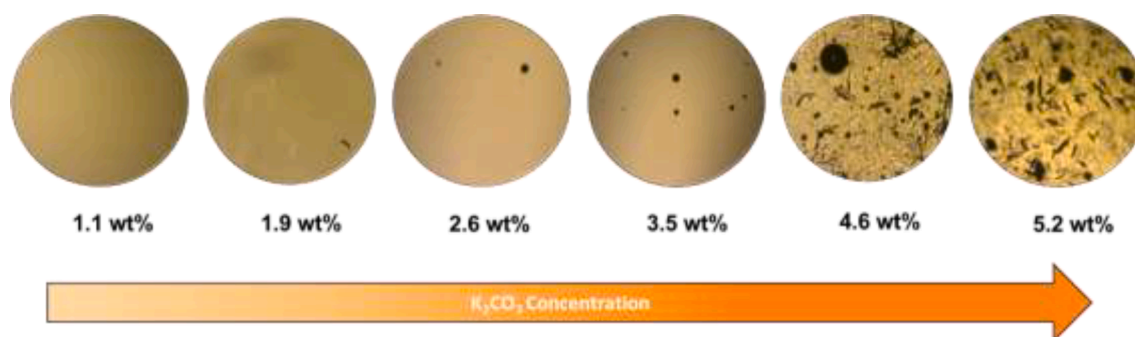


Fig. 5. Microscope image of IL solutions with different concentrations of  $K_2CO_3$  after cellulose dissolution. Condition: 85 wt% [mTBNH][OAc], 7.5 wt% water and 7.5 wt% cellulose at 353.2 K for 24 h.

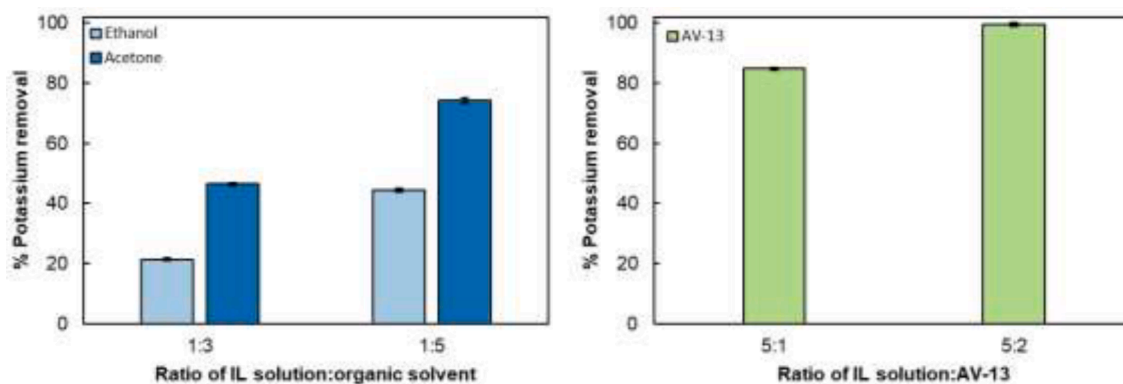


Fig. 6. Potassium removal efficiency of [mTBNH][OAc] systems composed of 64.2 wt% of IL, 3.5 wt%  $K_2CO_3$ , and 32.2 wt% water, at 298.15 K and atmospheric pressure.

rich phase. The first approach involved the addition of ethanol or acetone as an antisolvent to precipitate  $K_2CO_3$ , while the second method employed an inorganic ion exchange resin (AV-13) to remove the potassium cation. The results obtained from these two approaches are presented in Fig. 6.

Acetone as an antisolvent was found to remove up to 74.3% of potassium, whereas ethanol removed only up to 44.3%. The ratio of organic solvent to IL solution was found to directly impact potassium removal. Higher amounts of organic solvent led to greater removal of potassium, likely due to the lower solubility of the carbonate salt at higher concentrations of organic solvent. However, the high content of ethanol or acetone required (5 times the mass of the IL solution) can significantly increase the operating costs. Moreover, an additional step may be necessary to remove residual organic solvent from the IL phase.

Using AV-13 resin, it was possible to remove up to 99.6% of potassium with an IL solution to resin ratio of 5:2. The high efficiency of AV-13 was attributed to its well documented very high specificity towards  $K^+$  ions, which can be attributed to the resin's chemical composition and the diameter of its micropores, which act in a way similar to a selectivity filter. [31,32]

In contrast to ethanol or acetone, the separation of AV-13 from the IL solution can be accomplished easily through sieving, without the need for costly operating processes, and the resin can be regenerated by acid washing. Therefore, the resin approach is proposed as the preferred method for removing potassium from the IL phase, preventing its accumulation in subsequent IL recycling cycles.

#### 4. Conclusions

In this study, we have investigated the liquid-liquid equilibrium behaviour of [mTBNH][OAc] ionic liquid in the presence of water,

potassium carbonate and potassium phosphate salts at 298.2 K or 323.2 K and 102.8 kPa. Our results indicate that the nature of the salt has a direct impact on the phase behaviour, with phosphate anion inducing a stronger salting-out effect due to its higher entropy of solvation. The [mTBNH][OAc] partition coefficients and removal efficiency were also evaluated, revealing that all systems exhibit high partition coefficients up to 352.1, and the system with  $K_2CO_3$  showed the highest ionic liquid recovery rate of over 99.5%.

We also used the NRTL model to correlate the experimental data from the tie-lines, providing an accurate representation of the binodal curves and tie lines with a low RMSD value of less than 1.15%. Additionally, we demonstrated that residual potassium in the IL-rich phase can be efficiently removed using the inorganic ion exchange resin AV-13, which can be easily separated from the IL solution by sieving and regenerated by acid washing.

Overall, our findings suggest that the ATPS separation method using potassium salts is a promising approach for the efficient recovery of superbase ionic liquids from aqueous solutions. The knowledge gained from this study can contribute to the development of effective and sustainable processes for the production and recycling of ILs.

#### CRedit authorship contribution statement

**Filipe H.B. Sosa:** Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Visualization. **Ilkka Kilpeläinen:** Methodology, Writing – review & editing. **João Rocha:** Methodology, Writing – review & editing. **João A.P. Coutinho:** Conceptualization, Data curation, Writing – review & editing, Supervision, Funding acquisition.

## Declaration of Competing Interest

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.

## Data availability

No data was used for the research described in the article.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.fluid.2023.113857](https://doi.org/10.1016/j.fluid.2023.113857).

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