



# Extraction of acetic acid, glycolaldehyde and acetol from aqueous solutions mimicking pyrolysis oil cuts using ionic liquids



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## ABSTRACT

Value-added oxygenates, such as acetic acid (HAc), glycolaldehyde and acetol, are present in pyrolysis oil and its cuts in substantial amounts. This work describes the separation of these value-added oxygenates from artificial aqueous fractions of pyrolysis oil via liquid-liquid extraction. Three phosphonium ionic liquids (ILs), two imidazolium ILs and one benchmark organic mixture (40 wt% tri-*n*-octylamine in 1-octanol: TOA/1-octanol) were applied as solvents. Although suited as solvent for HAc and glycolaldehyde, the benchmark TOA/1-octanol showed a low acetol distribution coefficient (0.05), which makes it less suitable for use in an integrated oxygenates extraction process. Phosphonium ILs showed the highest affinities for HAc and glycolaldehyde, and reasonable affinity for acetol. However, none of these solvents could be applied to remove all oxygenates from the aqueous solution in a single extraction step, because of the difficulty of oxygenates evaporation from phosphonium ILs and the reactivity of glycolaldehyde with  $P_{666,14}[N(CN)_2]$  in the presence of HAc, as was confirmed by NMR. Based on the good affinity of the imidazolium ILs for acetol, a two-step extraction process was proposed where Hmim[B(CN)<sub>4</sub>] may be used to extract acetol and HAc in the first step and be regenerated by evaporation of the solutes, and  $P_{666,14}[Phos]$  may be applied to extract glycolaldehyde in the second step and be regenerated by back-extraction with water.

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## 1. Introduction

Due to the rising concerns on climate change, biomass as renewable resource has gained growing interest for production of bio-based fuels and chemicals. Pyrolysis oil (also known as bio-oil), the liquid product of fast pyrolysis (heating biomass in absence of oxygen to temperatures above 400 °C), has been applied as a renewable fuel for generation of heat and power [1]. Next to direct use of the oil as fuel, also separation and valorization of attractive chemicals present in the pyrolysis oil such as aromatics and sugars have been widely studied [2–5]. Within the pyrolysis oil some other value-added oxygenates are also present in substantial amounts, such as acetic acid (HAc, 12%), glycolaldehyde (13%) and acetol (7.4%) [6].

These oxygenates offer interesting commercial opportunities. Glycolaldehyde can be used as an effective meat-browning agent [7] or as fermentation feedstock for production of ethylene glycol [8]. HAc as an important chemical reagent is primarily employed in the production of cellulose acetate and polyvinyl acetate [9]. Additionally, acetol can promote various reactions (e.g. dehydra-

tion, hydrogenation, oxidation) and produce numerous products including propylene glycol, acrolein, acetone and furan derivatives [10].

Prior to further upgrading, these chemicals need to be isolated from the pyrolysis oil mixtures. Direct distillation of these oxygenates is not feasible due to the poor thermal stability of the pyrolysis oil [11], and direct extraction with an organic solvent is not attractive as a certain amount of the solvent ends up in the pyrolysis oil phase [12]. A potential initial step is to apply a water wash, and collect the polar oxygenates in the aqueous fraction. Upon water addition to the pyrolysis oil, 80–90% of the oxygenates can be extracted to the aqueous phase, based on their polarity [13]. An elegant alternative for water wash can be a thermal fractionation by employing a series of condensers operated at different temperatures to condense fractions of the pyrolysis vapors based on the boiling points of the species in the fractions. By careful control of the condenser temperatures, aqueous fractions containing up to 10% HAc and 8% acetol can be obtained directly from one of the condensers [14]. Because both methods are not highly selective, many other compounds with either similar polarity or boiling points are present in the mixtures as well.

Several methods have been investigated to separate specific oxygenates from the aqueous fractions of pyrolysis oil. Nanofiltration

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has been employed by Ford and coworkers to recover HAC, but the membrane was irreversibly damaged by the phenolics that were also present in the solutions [15]. Liquid-liquid reactive extractions using tertiary amines have been widely studied for HAC recovery from aqueous solutions [16–18]. In one single stage, about 84 wt % HAC was recovered with 40 wt% tri-*n*-octylamine in 2-ethyl-hexanol at room temperature from the aqueous fraction of pyrolysis oil with 3.33 wt% HAC in the mixture at a 1:1 solvent to feed ratio [17]. However, solvent regeneration via vacuum distillation results in the loss of 2-ethyl-hexanol which may co-evaporate with the solute [19].

Stradal and Underwood have invented a process to isolate glycolaldehyde from pyrolysis oil [20]. The process shown in Scheme 1 comprises several steps: (i) water extraction to produce a water soluble fraction of pyrolysis oil; (ii) water evaporation to reduce water content; (iii) multiple evaporation and fractionation steps to remove the low and high boiling components and further concentrate glycolaldehyde; (iv) precipitation of glycolaldehyde from methylene chloride. The separation steps of evaporation and distillations should be operated carefully to prevent reactions of glycolaldehyde, e.g. low temperature, vacuum pressure, short residence time at high temperature. Multiple evaporation and condensation steps are not economic and it appears better to selectively extract glycolaldehyde and recover it from the solvent.

De Haan and co-workers have studied extensively on isolation of glycolaldehyde from aqueous fractions of pyrolysis oil by liquid-liquid extraction [8,18,19,21]. High extraction efficiency of glycolaldehyde can be achieved via reactive extraction with primary amines, but the regeneration is challenging due to the high stability of the formed Schiff-base [21]. Physical extraction of glycolaldehyde with 1-octanol was also investigated, but low overall glycolaldehyde yield (17.2%, the percentage of its initial mass in the feed) was obtained from the proposed process, due to the low distribution coefficient of glycolaldehyde (0.25) [8]. Acetol was also co-extracted with 1-octanol, but the distribution coefficient of acetol was low as well (0.17). The other alternative is co-extraction of glycolaldehyde during reactive extraction of HAC with TOA in 2-ethyl-hexanol [18]. High HAC recovery yield (80%) was obtained but less than 10 wt% of glycolaldehyde (the percentage of its initial amount in the feed) was extracted due to the low distribution coefficient of glycolaldehyde (<0.20). Thus, exploring of new solvents with higher distribution coefficients of these oxygenates may bring new process options with a smaller impact on the environment.

Ionic liquids (ILs), known as environmentally friendly solvents, have been proposed to be used for liquid-liquid extractions, e.g.

separation of aromatics from aliphatics [22–24] or from sugar solutions [3,5], recovery of precious metals for recycling [25]. Their negligible vapor pressure and high thermal stability allow ILs to be recovered from the extract by solutes evaporation, which uses potentially less energy than recovery of low boiling organic solvents where large amount of solvents are typically evaporated [3]. Moreover, the extractability of the solutes can be enhanced by tuning the combination of cations and anions. ILs have shown potential for extraction of acids (e.g. HAC, lactic acid, amino acid) from aqueous solutions [26–32]. However, there is no report on utilization of ILs to extract oxygenates from aqueous solutions of pyrolysis oil.

In this work, the feasibility and reusability of ILs to extract the oxygenates acetol, HAC and glycolaldehyde from the model aqueous solutions of pyrolysis oil is investigated. Three phosphonium ILs have been studied in this work due to their hydrophobicity and high affinity for acids [30,33]. Two other commercially available hydrophobic imidazolium ILs with tetracyanoborate anion are also investigated, as they have shown potential in extraction of polar compounds [34], and the solvent recovery may be straightforward through solute evaporation. The names and abbreviations of the studied ILs are shown in Table 1 and the structures of ILs and the oxygenates are drawn in Scheme 2. The organic solvent 40 wt% TOA in 1-octanol is also studied as comparison, because of its high distribution of HAC [30]. 1-octanol is used as diluent in this work, since it is available in the lab and has similar distribution coefficient for HAC as 2-ethyl-1-hexanol [17].

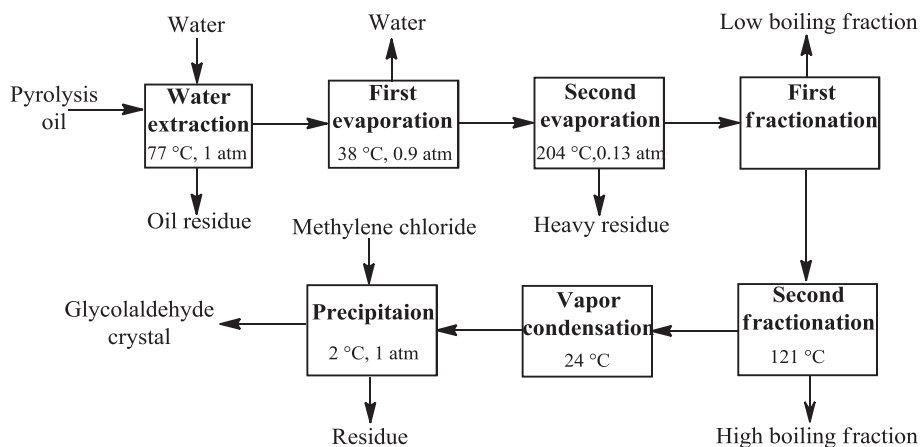
## 2. Experimental

### 2.1. Materials

Acetic acid (>99.7%), acetol (hydroxyacetone, 90%), glycolaldehyde dimer, tri-*n*-octylamine (98%), 1-octanol (>99%), toluene (>99.8%) and dimethyl sulfoxide-*d*<sub>6</sub> (>99.96%, DMSO) were purchased from Sigma Aldrich. The phosphonium ILs P<sub>666,14</sub>Cl, P<sub>666,14</sub>[N(CN)<sub>2</sub>] and P<sub>666,14</sub>[Phos] were obtained from Iolitec with a purity >95%. The imidazolium ILs Hmim[B(CN)<sub>4</sub>] and Omim[B(CN)<sub>4</sub>] were purchased from Merck with a purity >98%.

### 2.2. Liquid-liquid extraction

Three single solute solutions (10 wt% acetol, 10 wt% HAC and 5 wt% glycolaldehyde solution, respectively) and one mixed solutes solution (with 10 wt% acetol, 10 wt% HAC and 5 wt% glycolaldehyde together in milli-Q water) were prepared as feed solutions.



**Scheme 1.** Glycolaldehyde isolation process designed by Stradal and Underwood. The missing temperatures and pressures in the scheme are not given in Ref. [20].

**Table 1**  
Names and abbreviations of solvents studied in this work.

Name of solvents	Abbreviations
Trihexyltetradecylphosphonium chloride	P <sub>666,14</sub> Cl
Trihexyltetradecylphosphonium dicyanamide	P <sub>666,14</sub> [N(CN) <sub>2</sub> ]
Trihexyltetradecylphosphonium bis-2,4,4-(trimethylpentyl)phosphinate	P <sub>666,14</sub> [Phos]
1-hexyl-3-methylimidazolium tetracyanoborate	Hmim[B(CN) <sub>4</sub> ]
1-octyl-3-methylimidazolium tetracyanoborate	Omim[B(CN) <sub>4</sub> ]
40 wt% tri- <i>n</i> -octylamine in 1-octanol	TOA/1-octanol

Extraction experiments were conducted by adding 2 g feed solution and 2 g solvent in glass vials which were then introduced in a shaking bath at 200 rpm at the desired temperatures (25 < T < 60 °C). After 18 h shaking, the phases were allowed to settle down for 2 h while keeping the correct temperature. The raffinate and extract phases were then separated and weighed. The raffinates were analyzed with HPLC to obtain the concentrations of acetol, HAc and glycolaldehyde. The contents of these compounds in the extracts were calculated by mass balance [3]. Water concentration in the pure solvents and the extract phases was measured with Karl Fisher titration.

For the study on the mutual influence of HAc and glycolaldehyde on extraction efficiency, as well as on the solvent influence five feed solutions, i.e. 0.01–0.2 M (0.15–1.21 wt%) glycolaldehyde solutions were prepared by dissolving varying amounts of glycolaldehyde in milli-Q water, to which solvent phase containing HAc was added. The solvent phases were 0.5 M P<sub>666,14</sub>[N(CN)<sub>2</sub>] in toluene with five different concentrations of HAc (0–1.0 M, 0–6.2 wt%). HAc was added to the solvent mixture instead of to the feed, in order to simplify the experimental procedure, i.e. 5 feeds and 5 solvents were prepared instead of 25 feeds and 1 solvent. To prepare the solvent, in the first step, IL was diluted to 0.5 M (29 wt%) in toluene, then certain amount of HAc was added to IL/Toluene mixture to obtain the desired concentrations. The liquid-liquid extractions were carried out by contacting 2 mL solvents with 10 mL feeds at 40 °C. By combining different feed and solvent, the ratios of glycolaldehyde to IL and to HAc were tuned. The

concentrations of the HAc and glycolaldehyde in the aqueous feed were recalculated, based on the initial amount of glycolaldehyde and water in the feed and the added HAc in the solvent. The concentrations of HAc and glycolaldehyde in the raffinates were analyzed with HPLC.

### 2.3. Samples preparation for NMR analysis

Four mixtures were prepared for the analysis of <sup>1</sup>H NMR and <sup>13</sup>C NMR, including HAc + glycolaldehyde, P<sub>666,14</sub>[N(CN)<sub>2</sub>] + glycolaldehyde, HAc + P<sub>666,14</sub>[N(CN)<sub>2</sub>] and HAc + glycolaldehyde + P<sub>666,14</sub>[N(CN)<sub>2</sub>]. In order to keep similar conditions as extraction experiments, after being diluted in DMSO-*d*<sub>6</sub>, these mixtures were mixed at 40 °C for 18 h in a shaking bath at 200 rpm. Then all samples were analyzed with a Bruker NMR machine to obtain the <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra.

### 2.4. IL regeneration

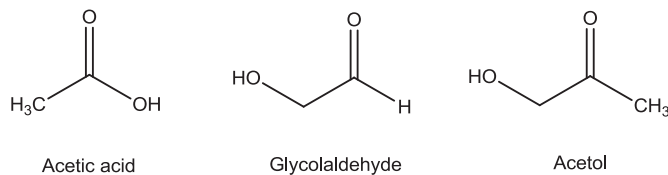
After extraction from the mixed solutes feed, the ILs P<sub>666,14</sub>Cl, P<sub>666,14</sub>[N(CN)<sub>2</sub>] and P<sub>666,14</sub>[Phos] were regenerated from their corresponding extract phases (10 g) by evaporating the solutes at 100 °C and 20 mbar in a 100 mL flask for 1 h while bubbling the flask with N<sub>2</sub> to avoid condensation in the neck of the flask. The regenerated P<sub>666,14</sub>[Phos] was then used for the second round of extraction from a fresh feed solution.

After extraction from the mixed solutes feed with Hmim[B(CN)<sub>4</sub>], this IL was recovered at 60 °C and 20 mbar for 30 min, and the regenerated IL was reused as solvent to extract oxygenates from the fresh feed. This IL was recycled three times for four extractions in total. The raffinate after each extraction was analyzed with HPLC to obtain the concentrations of the oxygenates. The contents of these compounds in the extracts were calculated by mass balance.

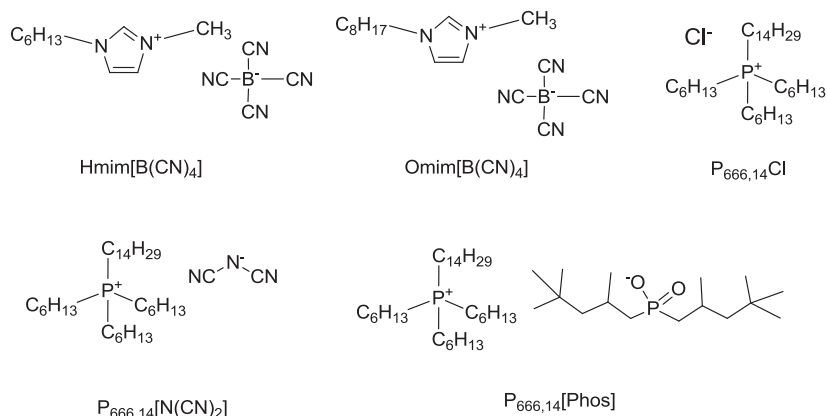
### 2.5. Analysis

High performance liquid chromatography (HPLC, Agilent 1200 system) was employed to analyze the concentrations of HAc,

Oxygenates:



ILs:



**Scheme 2.** Structures of the oxygenates and the studied ILs.

glycolaldehyde and acetol in the raffinates. HPLC was equipped with a Hi-Plex-H column operated at 60 °C and a refractive index detector at 55 °C (RID, relative standard deviation from 5 measurements: 1.2%), using mobile phase 5 mM sulfuric acid at a flow rate of 0.6 mL/min. Water uptake in the pure solvents and the extract phases was determined with Karl Fisher titration (titrant: hydranal composite 5, Metrohm 787 KFTitrino) and the relative standard deviations from triplicate measurements were lower than 8%. A solution of methanol and dichloromethane (3:1, volumetric ratio) was used as solvent.

## 2.6. Definitions

The extraction efficiency of the solvents is designated as distribution coefficient of solutes in solvents which is defined in Eq. (1):

$$D_i = \frac{x_i^I}{x_i^{II}} \quad (1)$$

where  $x_i^I$  and  $x_i^{II}$  represent the weight fraction of solute  $i$  in phase I (an IL or TOA/1-octanol phase) and phase II (the aqueous raffinate phase) respectively.

## 2.7. COSMO-RS predictions

COSMO-RS, the conductor-like-screening-model for real solvents, which is based on the molecular quantum chemical calculations of the individual species in the system, can be used for prediction of the equilibrium thermodynamic properties of pure components and mixtures [3,35,36]. In this work, the turbomole program package (version 7.0) was used to predict the distributions of the molecular surface charge densities ( $\sigma$ -profiles). The software tool COSMOthermX (C30-1501) was applied to predict the partition coefficients of the oxygenates in octanol and water ( $\log P$ ).

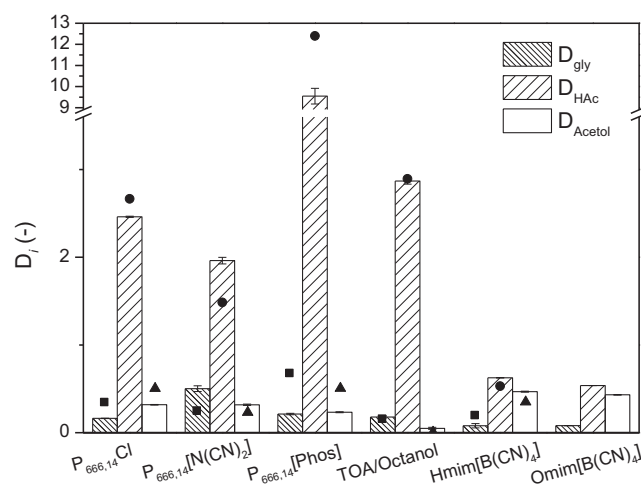
## 3. Results and discussion

### 3.1. Solvent efficiency for extraction of oxygenates from artificial aqueous fraction of pyrolysis oil

Liquid-liquid extraction experiments were carried out to study the extraction efficiency of the solvents in the removal of glycolaldehyde, HAc and acetol from the artificial aqueous mixture at room temperature (25 °C). To study the competitive effect of the solutes on extraction, both single solute solutions and a mixed solutes solution were applied as feeds. The equilibrium distribution coefficients of the solutes ( $D_i$ ) for all the solvents are presented in Fig. 1. The results of  $D_{\text{HAc}}$  for  $P_{666,14}$ [Phos] and TOA/1-octanol are in the same order of magnitude with what was reported by previous studies [17,29,30,33], confirming the reliability of the data in this work.

By comparing the extractions from the single solute solutions ( $D_i^{\text{Single}}$  shown as symbols) with the extractions from the mixed solutes solution ( $D_i^{\text{Mix}}$  shown as column bars), it is found that for all three solutes,  $D_i^{\text{Single}}$  was either higher or similar than/as  $D_i^{\text{Mix}}$  for most studied solvents, indicating that in most solvents, the three solutes were competing with each other in the extraction. However, for  $P_{666,14}$ [N(CN)<sub>2</sub>] the result showed an opposite trend, with  $D_i^{\text{Single}}$  being lower than  $D_i^{\text{Mix}}$ , indicating that the solutes were mutually enhancing their extractability.

It is observed from Fig. 1 that all the solvents had the strongest affinity for HAc, whereas their affinity for glycolaldehyde and acetol were significantly lower. For  $P_{666,14}$ [Phos],  $D_{\text{HAc}}$  was 42–45



**Fig. 1.** Distribution coefficients ( $D_i$ ) of glycolaldehyde, HAc and acetol as obtained in liquid-liquid equilibria at 1:1 solvent to feed ratio (mass based) at 25 °C. Column bars for mixed solutes solution; Symbols for single solute solutions. (■):  $D_{\text{gly}}$ , (●):  $D_{\text{HAc}}$ , (▲):  $D_{\text{Acetol}}$ .

times higher than  $D_{\text{Acetol}}$  and  $D_{\text{gly}}$ , and around 10 times in the case of  $P_{666,14}\text{Cl}$ . This observation is related to the polarity of the solutes: HAc > glycolaldehyde > acetol, deduced from the  $\sigma$ -profiles of these solutes shown in Fig. S1 in the electronic supplementary information (ESI). The stronger polar molecular surfaces of HAc correspond with the hydrogen bond donating capabilities and thus are more likely to form hydrogen bonds with the anion of ILs. The high  $D_{\text{HAc}}$ , attributed to the strong hydrogen bonding interaction between acid and the solvents has also been reported in the literature [30].

The similar  $\sigma$ -profiles (see Fig. S1) of glycolaldehyde and acetol indicate that they exhibit alike surface polarities, which results in comparable  $D_{\text{gly}}$  and  $D_{\text{Acetol}}$  for the phosphonium ILs. However, it was not experimentally observed for the imidazolium ILs. Because for the imidazolium ILs the distribution coefficients of the solutes are in the same order as the COSMO-RS predicted  $\log P$  values (the partition coefficient of the solutes in 1-octanol/water biphasic system): glycolaldehyde ( $\log P = -1.103$ ) < Acetol ( $\log P = -0.584$ ) < HAc ( $\log P = -0.266$ ), it is suggested that in the oxygenates extraction with these two imidazolium ILs, the solute hydrophobicities (expressed as  $\log P$ ) are the governing factor. The lowest  $\log P$  of glycolaldehyde indicates that this solute has very strong affinity towards water and thus it is the most difficult one to be extracted. Although the imidazolium ILs have a hydrophobic character, preferring HAc over acetol over glycolaldehyde in their hydrophobic order, they also contain the hydrogen bond accepting CN-functionality. A slightly higher distribution was observed with Hmim[B(CN)<sub>4</sub>] than with Omim[B(CN)<sub>4</sub>] for all solutes, which may suggest that the functional group density (mol CN per kg solvent) of the hydrogen bond accepting group is positively affecting the extraction and a shorter alkyl chain in the cations results in a higher distribution.

The distribution of HAc for the studied ILs follows the order: Phos > Cl > N(CN)<sub>2</sub> > B(CN)<sub>4</sub>, which is in line with the polarities of the anions, based on their  $\sigma$ -profiles shown in Fig. S2 in the ESI. The remarkably high  $D_{\text{HAc}}$  for  $P_{666,14}$ [Phos] is suspected to be at least partly due to the proton transfer from the HAc to the Phos anion, resulting in a long chain hydrophobic phosphinic acid and phosphonium acetate. Moreover, it is suggested in the literature that the IL with Phos anion could form complexes with acid and water [33], which may enhance the extraction of HAc, and this probably does not happen for ILs with other anions.

The organic solvent TOA/1-octanol showed comparable extraction efficiencies for HAC and glycolaldehyde with phosphonium ILs (except for  $P_{666,14}$ [Phos] which showed a much higher extraction efficiency), and even higher than imidazolium ILs. But on the other hand,  $D_{\text{Acetol}}$  was extremely low ( $0.05 \pm 0.01$ ) in TOA/1-octanol, which is comparable with the literature where 40 wt% TOA in 2-ethyl-1-hexanol were applied as solvents [17]. This suggests TOA/1-octanol exhibits a high selectivity of HAC over acetol, but this also implies a poor extractability of acetol.

The water concentrations in the pure solvents and the extract phases measured with Karl Fisher are shown in Table 2. It is seen that the water solubility decreased in the extract phases of  $P_{666,14}\text{Cl}$  and  $P_{666,14}$ [Phos], compared with the values in the pure ILs, which is in line with the observations from other researchers [37]. It is suggested that the high water uptake of  $P_{666,14}$ [Phos] is due to the formation of water-IL clusters, which break with increasing amounts of extracted solutes, and because of that the water solubility in the solvents decreases after extraction [37]. The data in the last column in Table 2 are from the reference [30] where the water solubilities in the extract phases are similar as those in the pure solvents. This is because of the relatively low concentration of HAC (1 wt%) in the feed, resulting in low amount of solute in the extract phase, and hence negligible influence on water solubility. On the contrary, for the other three solvents, the water concentration of the organic phase increased slightly after extraction. This may result from the strong interaction of the oxygenates with water which was pulled by oxygenates to the organic phase. The water in the extract phase has to be evaporated in the process of solute recovery from the extract phase by evaporation, which will use extra energy. Thus,  $P_{666,14}$ [N(CN)<sub>2</sub>] is the preferable solvent with respect to the water concentration in the extract phase.

With the aim of extracting all three compounds in an integrated process, the phosphonium ILs are the most suitable solvents for oxygenates extraction, as they have high affinity towards not only HAC but also the most difficult extracted solute glycolaldehyde. TOA/1-octanol has very low extraction efficiency for acetol, thus it is less suited for use in an integrated extraction process. However, as a benchmark solvent, it was also studied together with phosphonium ILs for the temperature influence on the extraction efficiency.

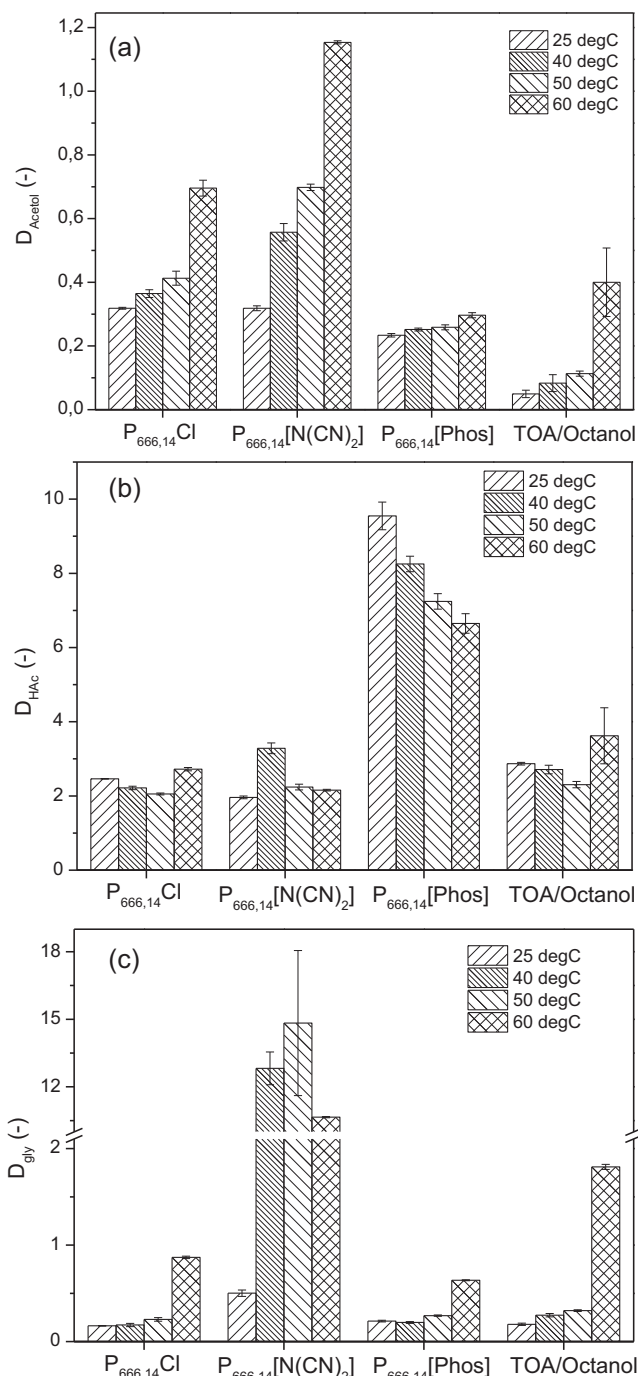
### 3.2. Temperature influence on extraction efficiency

The measured  $D_i$  at four different temperatures are given for the various solvents in Fig. 2a–c. From Fig. 2 it follows that the temperature influence differs for varying solutes. It is shown in Fig. 2a that  $D_{\text{Acetol}}$  gradually increased from 25 to 50 °C, which might be attributed to the weaker intermolecular interactions (e.g. hydrogen bonding) at higher temperature. The considerable increase between 50 °C and 60 °C might be due to the instability of acetol

**Table 2**

Water concentrations of the pure solvents and the extract phases at 1:1 solvent to feed ratio at 25 °C.

Extract phases	Water concentration in pure solvents (wt%)	Water concentration in extract phase (wt%)	Water concentration in extract phase from Ref. [30] (wt%)
$P_{666,14}\text{Cl}$	14.4 [33]	8.85	13.6
$P_{666,14}$ [N(CN) <sub>2</sub> ]	3.31 [33]	3.63	3.9
$P_{666,14}$ [Phos]	14.4 [33]	6.82	14.1
Hmim[B(CN) <sub>4</sub> ]	4.89	5.91	Not available
TOA/1-octanol	2.03	4.87	2.5



**Fig. 2.** The distribution coefficients of the solutes at different temperatures in phosphonium ILs and TOA/1-octanol. (a)  $D_{\text{Acetol}}$ ; (b)  $D_{\text{HAC}}$ ; (c)  $D_{\text{gly}}$ .

at higher temperature where acetol can be converted to other compounds [38].

No clear trend of temperature effect on  $D_{\text{HAC}}$  was observed for most solvents from Fig. 2b, but it is obviously decreasing for  $P_{666,14}$ [Phos] with the temperature increasing. This suggests that at high temperature the hydrogen bonding interaction was weakened, and probably also the level of organization of the hydrophilic clusters, which is supported by the decreasing water content in the IL phase with increasing temperature [33].

The general trends of the temperature influence on  $D_{\text{gly}}$  are the same as those observed for  $D_{\text{Acetol}}$  for the solvents  $P_{666,14}\text{Cl}$ ,

$P_{666,14}[\text{Phos}]$  and TOA/Octanol. Above 50 °C there is a remarkable increase of the distribution coefficient, which most likely is the result of thermal instability of glycolaldehyde especially in basic solutions such as TOA/1-octanol. However, for  $P_{666,14}[\text{N}(\text{CN})_2]$  the distribution already increases strongly between 25 and 40 °C, and a maximum was observed at 50 °C, and then drops again at further temperature increase to 60 °C. Compared with the increase in  $D_{\text{gly}}$  for other solvents, the increase was considerable (26 times vs 1.5 times for TOA/1-octanol) from 25 °C to 40 °C. Correspondingly, the glycolaldehyde extraction yield increased from 39% to 94%. In order to understand better the phenomena occurring during the extraction, a more detailed analysis was performed using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

### 3.3. Extraction mechanism

To elucidate on the phenomena and the possible mechanism of glycolaldehyde extraction with  $P_{666,14}[\text{N}(\text{CN})_2]$ , a series of extraction experiments was carried out with various ratio of HAC to IL and glycolaldehyde to IL at 40 °C, followed by the NMR analysis.

The raffinate concentrations of glycolaldehyde ( $x_{\text{gly}}$ ) and HAC ( $x_{\text{HAC}}$ ) are displayed in Fig. 3a and b, respectively, for the various IL:glycolaldehyde ratios. The feed concentrations are indicated with open symbols and the raffinate concentrations with closed symbols. It can be seen in Fig. 3a that for all IL:glycolaldehyde ratios, the raffinate concentration  $x_{\text{gly}}$  reduced with increasing

initial HAC concentration, and when no HAC was present ( $\blacklozenge$ ), the  $x_{\text{gly}}$  in the raffinates were comparable with that in the feed, implying almost no glycolaldehyde was extracted. From this trend, it is concluded that HAC enhances the glycolaldehyde extraction.

In Fig. 3b, the  $x_{\text{HAC}}$  from the same experiments are displayed, and here the feed concentrations with open symbols are displayed as the most right series, while going from right to left in the figure, the IL:glycolaldehyde is reduced, also increasing thus the glycolaldehyde to HAC ratio. Also in this figure, a reduction of HAC concentration in the raffinate was observed with increasing initial concentration of glycolaldehyde, from which it is concluded that both HAC and glycolaldehyde are mutually enhancing their extractability.

Furthermore, since the strong effect of temperature was shown only for  $P_{666,14}[\text{N}(\text{CN})_2]$ , it is suspected that this solvent plays a role in the reaction/extraction mechanism, and to study this role, the reaction between glycolaldehyde and  $P_{666,14}[\text{N}(\text{CN})_2]$  was justified by NMR analyses. The  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra of four mixtures are shown in Figs. S3 and S4 in the ESI. It is observed from the  $^{13}\text{C}$  NMR spectra in Fig. S3a–c that no peak diminished or appeared in all of the spectra with only two components present, i.e. glycolaldehyde + HAC, glycolaldehyde +  $P_{666,14}[\text{N}(\text{CN})_2]$  or HAC +  $P_{666,14}[\text{N}(\text{CN})_2]$ , implying no reaction would take place when any of two components were mixed. However, when mixing HAC, glycolaldehyde and IL all together, it is shown in the  $^{13}\text{C}$  NMR spectra in Fig. S3d that the signal of aldehyde diminished and new signal characteristic for ester groups at  $\delta = 165$  and some other unknown peaks at  $\delta = 120\text{--}135$  and  $\delta = 72\text{--}88$  emerged. In the  $^1\text{H}$  NMR spectra in Fig. S4c also newly appeared peaks were observed at  $6.5 < \delta < 8.5$ . Both  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR confirm the formation of new compounds and this only happens when all three components are present in the mixture.

Due to the low intensity and resolution of the NMR signals, it is difficult to determine the structure of the new formed compounds and the reaction mechanism is not clearly known at this stage. Also a clear stoichiometric relation between the IL, the extracted HAC and glycolaldehyde was not found. However, based on our results, possible reactions are proposed and shown in the ESI. It is suspected that the negatively charged N in the anion of IL acts as a nucleophile, attacking the carbonyl carbon from the glycolaldehyde that is activated in the presence of acid, and form a new C–N single bond. The new peak of ester group suggests that the esterification reaction was improved. Furthermore, HAC appears to promote this reaction which is likely in the role of an acid catalyst.

### 3.4. Recycling of ILs

To design a sustainable extraction process, solvent recovery, in this case thus IL recovery is an essential step. Therefore, the recovery of four ILs (see Table 3) is studied by evaporating the oxygenates from corresponding extract phases under vacuum conditions as described in Experimental Section 2.4.

The IL recoverability is presented as the percentage of evaporated solutes (oxygenates and water) based on the initial mass of solutes that was present in the extracts. Assuming all the water could be evaporated and thus the remaining solutes after evaporation were all considered as oxygenates, the percentage of the evaporated oxygenates were then calculated based on the initial mass of oxygenates in the extracts. The results and the operating conditions are shown in Table 3. It can be seen that removal of the solutes from all of the phosphonium ILs was very difficult by evaporation, and only a fraction of the oxygenates was removed, which is likely due to the strong interaction of the oxygenates (especially HAC) with phosphonium ILs and the reactive extraction of  $P_{666,14}[\text{N}(\text{CN})_2]$  with glycolaldehyde.

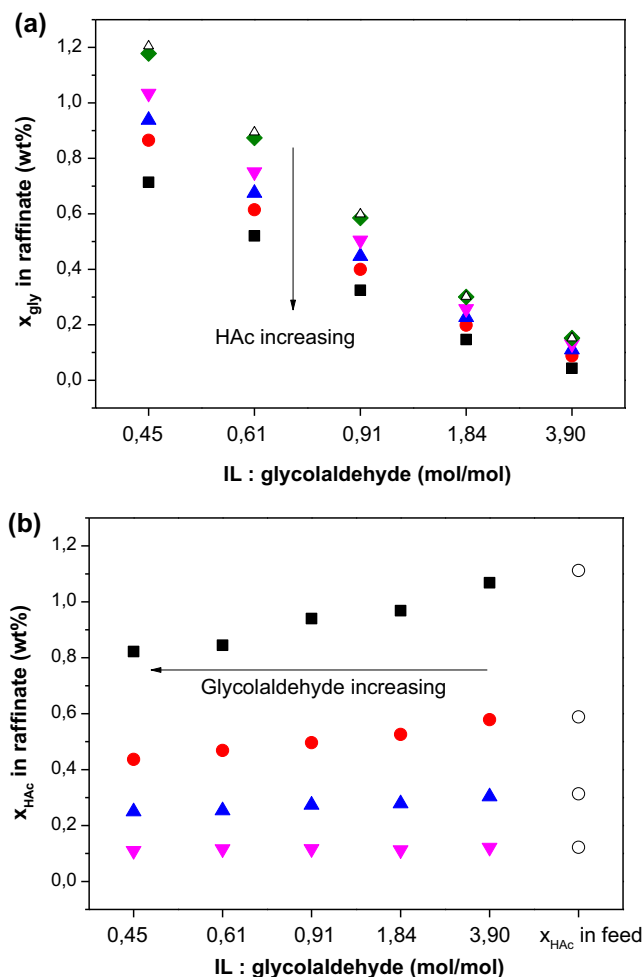


Fig. 3. The concentration of glycolaldehyde (a) and HAC (b) in the feeds (hollow symbols) and raffinates (full symbols) after extraction with  $P_{666,14}[\text{N}(\text{CN})_2]$ . The HAC:IL (mol/mol) are 2.10:1 ( $\blacksquare$ ), 1.10:1 ( $\bullet$ ), 0.56:1 ( $\blacktriangle$ ), 0.22:1 ( $\blacktriangledown$ ) and 0:1 ( $\blacklozenge$ ). Symbol  $\triangle$ :  $x_{\text{gly}}$  in feed;  $\circ$ :  $x_{\text{HAC}}$  in feed.

**Table 3**  
Evaporation of the extracted solutes at 20 mbar with N<sub>2</sub> flushing.

Solvents	P <sub>666,14</sub> Cl	P <sub>666,14</sub> [N(CN) <sub>2</sub> ]	P <sub>666,14</sub> [Phos]	Hmim[B(CN) <sub>4</sub> ]
Percentage of evaporated oxygenates and water based on their initial mass in the extracts (wt%)	86.3	70.7	70.3	100
Percentage of evaporated oxygenates based on the initial mass of oxygenates in the extracts (wt%)	74.0	62.0	51.5	100
Temperature (°C)	100	100	100	60
Heating time (h)	1	1	1	0.5

The relatively low distribution coefficients of HAc for Hmim[B(CN)<sub>4</sub>] indicate less strong interactions than for phosphonium ILs, and it is seen that the evaporative recovery achieved 100% at relatively benign conditions. Considering the thermal instability of the glycolaldehyde and acetol, the recovery method needs to be optimized towards lower temperature, which could be achieved by lowering the pressure or increasing the evaporation time.

The regenerated P<sub>666,14</sub>[Phos] and Hmim[B(CN)<sub>4</sub>] were chosen for studying the solvent reusability by performing the second cycle of extraction from the fresh mixed solutes feed. When extracting with the regenerated P<sub>666,14</sub>[Phos],  $D_i$  decreased significantly (e.g. around half for glycolaldehyde), suggesting that the remained solutes in the regenerated IL have strong negative effect on the next extraction cycle. When extracting with the regenerated Hmim[B(CN)<sub>4</sub>], it was found out that the extraction efficiency of the recycled ILs was similar with the fresh ILs. Hmim[B(CN)<sub>4</sub>] was used in a total of four extraction cycles with a stable  $D_i$  for all four cycles as shown in Fig. 4. This confirms the thermal stability of the IL and the stable extraction performance of the recycled IL, and the suitability of vacuum evaporation to recover the solutes for Hmim[B(CN)<sub>4</sub>] recovery.

For the ILs that could not be regenerated by direct evaporation, the use of a back-wash is suggested. For example, in the case of glycolaldehyde, with a distribution coefficient below unity, the back-wash with water may regenerate the solvent at the cost of an additional operation. For HAc, the regeneration through back-wash is less effective due to the higher distribution. Therefore, a combination of extraction steps is suggested.

To avoid difficulties, the irreversible reactive extraction of glycolaldehyde with P<sub>666,14</sub>[N(CN)<sub>2</sub>] should be omitted. As  $D_{\text{Acetol}}$  for Hmim[B(CN)<sub>4</sub>] was 3–10 times higher than that for the studied solvents and other reported solvents (e.g. 1-octanol, 2-ethyl-1-hexanol and TOA) [8,19], the required solvent to feed ratio for Hmim[B(CN)<sub>4</sub>] would decrease significantly to achieve the same recovery target. Also P<sub>666,14</sub>[Phos] has a 2–4 times higher  $D_{\text{gly}}$  than

other studied solvents when extracting from single solute solution. Although TOA/1-octanol has a higher  $D_{\text{HAc}}$  than Hmim[B(CN)<sub>4</sub>] and thus less solvent would be required for HAc extraction, it is not necessary to use TOA/1-octanol for HAc extraction in a separate step, because HAc can be co-extracted when extracting acetol with Hmim[B(CN)<sub>4</sub>]. Thus, a two-step extraction was proposed where HAc and acetol are extracted in the first step with Hmim[B(CN)<sub>4</sub>] and glycolaldehyde is removed in the second step with P<sub>666,14</sub>[Phos]. HAc and acetol will then be recovered through vacuum evaporation and glycolaldehyde via water back-extraction.

#### 4. Conclusions

From the comparison of the distributions in the extraction stage, it was found that the benchmark solvent TOA/1-octanol has the lowest extraction efficiency for acetol, and phosphonium ILs the highest. However, due to occurring reactions and difficult regenerations, the phosphonium ILs cannot be applied for extraction of all oxygenates at once. In absence of HAc, however, P<sub>666,14</sub>[Phos] shows the highest glycolaldehyde distribution coefficient and can be regenerated by a water wash. This step can follow an initial extraction of HAc and acetol by Hmim[B(CN)<sub>4</sub>], which was shown to have the highest acetol distribution coefficient and could be completely thermally regenerated. Thus, a two-step extraction is proposed by employing Hmim[B(CN)<sub>4</sub>] in the first step to extract acetic acid and acetol, and using P<sub>666,14</sub>[Phos] in the second step to remove glycolaldehyde, followed by recovery of Hmim[B(CN)<sub>4</sub>] through solute evaporation and recovery of P<sub>666,14</sub>[Phos] via water back-extraction.

#### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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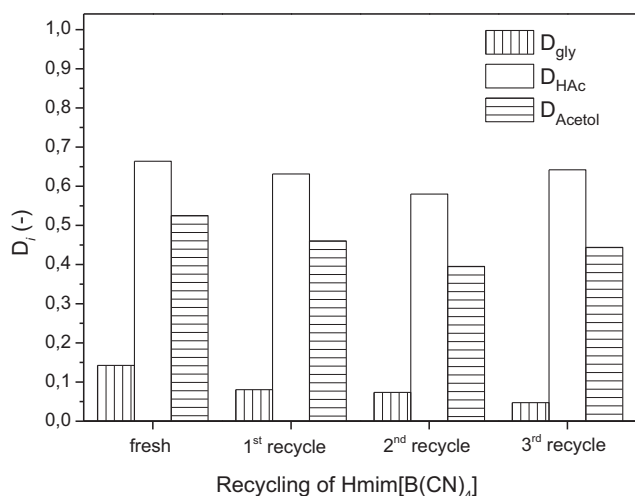
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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2016.10.023>.

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**Fig. 4.** Distribution coefficients of the solutes for the recycled Hmim[B(CN)<sub>4</sub>].

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