



Extraction of volatile fatty acids from fermented wastewater



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ABSTRACT

Valorization of wastewater streams can be done by fermentation to produce volatile fatty acids (VFAs) which are applied as platform chemicals for synthesis of value-added chemicals. Since VFA concentration in fermented wastewater is very low (~1 wt%) and fermented wastewater contains considerable amounts of dissolved salts, recovery of VFAs from fermented wastewater is challenging. To study the potential of some ionic liquids compared to traditional solvents for extraction of VFAs from fermented wastewater, a detailed study on the effects of various salt-originating ions on VFA extraction was performed. Ion exchange and intermolecular interactions (e.g. hydrogen bonding) were found to be responsible for extraction of VFAs. The presence of salts (e.g. KCl) resulted in extraction of acidic forms of salt-originating anions (e.g. $\text{H}^+ + \text{Cl}^-$). 20 wt% trioctylamine (TOA) in n-octanol (representing conventional solvents) and $[\text{P}_{666,14}][\text{Phos}]$ (an ionic liquid) were found to be the most promising VFA-extracting solvents. Their maximum VFA loadings while being in equilibrium with an artificial fermented wastewater were determined by performing cross-current extractions. $[\text{P}_{666,14}][\text{Phos}]$ achieved a higher maximum VFA loading which enables it to deliver a much more concentrated VFA stream at a lower solvent to feed ratio (S/F).

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1. Introduction

Due to rising concerns on depletion of easily accessible petroleum resources over the next decades, production of bio-based chemicals is gaining interest. Several major routes have been proposed to produce bio-based chemicals among which fermentation has gained the interest of many researchers, and much attempt has been made to improve the efficiency of fermentation-based processes [1]. Production of various groups of chemicals through fermentation has been reported in the literature. Many studies have focused on production of carboxylic acids through fermentation, as carboxylic acids are major platform chemicals for synthesis of value-added chemicals [2–5]. Volatile fatty acids (VFAs) are versatile carboxylic acids utilized in production of bio-plastic and bio-energy [1,6–7]. However, synthesis of value-added chemicals starting with production and purification of VFAs in an economically viable process is not straightforward. An important obstacle is the low concentration of VFAs in fermentation broths, which makes separation and purification of VFAs challenging.

Several separation techniques have been proposed to recover VFAs from aqueous solutions such as straight distillation,

extractive distillation, membrane filtration and crystallization [8–13]. However, due to the low concentration of VFAs in fermented wastewater, any separation technique attempting to recover VFAs by removing the water content of fermented wastewater is not economical. Therefore, affinity separation techniques with affinity for VFAs are considered as the only practical techniques to recover VFAs from fermented wastewaters. Preferentially, the separating agents used for affinity separation target the VFA molecules while minimizing water removal. Liquid–liquid extraction is one of the most applied affinity separation techniques, and with a proper choice of solvent, it can enable effective recovery of VFAs from dilute solutions in an energy efficient manner [14].

Traditional solvents used for extraction of organic acids from aqueous solutions include alcohols, ketones, ethers, aliphatic hydrocarbons, organophosphates, and aliphatic amines [8,15–18]. In the recent extraction literature, ionic liquids have been reported for extraction of VFAs, and some are shown to be superior to conventional solvents in terms of extraction efficiency from idealized aqueous solutions containing only acids and water [19–23].

Fermented wastewater contains less VFA compared to a fermentation broth purposely made for VFA recovery, as the carbon content of wastewater prior to fermentation is much lower. Furthermore, fermented wastewaters are not ideal aqueous solutions and typically contain significant amounts of various dissolved salts. Na^+ , K^+ , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, Cl^- , and SO_4^{2-} are the most common ions

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Nomenclature

MCFAs	medium chain fatty acids	TOA	trioctylamine
VFAs	volatile fatty acids	[P _{666,14}][Cl]	triethyl(tetradecyl)phosphonium chloride
HLa	lactic acid	[P _{666,14}][Br]	triethyl(tetradecyl)phosphonium bromide
HAc	acetic acid	[P _{666,14}][Phos]	triethyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate
HPr	propionic acid	[P _{666,14}][N(CN) ₂]	triethyl(tetradecyl)phosphonium dicyanamide
HBu	butyric acid		
Ac ⁻	acetate		

originating from the dissolved salts present in fermented wastewater (see Table 1 for typical composition of fermented wastewater). Due to the low concentration of VFAs and the presence of salt-originating ions, the typical pH of fermented wastewater ranges from 4 to 6. How the presence of these ions affects extraction of VFAs using ionic liquids and the traditional solvent trioctylamine (TOA) in n-octanol was the main research question investigated here.

For this study, an artificial fermented wastewater resembling an actual fermented wastewater was prepared according to the composition shown in Table 1. Next to extraction studies with this artificial fermented wastewater, several simpler model solutions were also prepared to examine the effects of salt-originating ions on extraction of VFAs. The study with the artificial fermented wastewater included multi-stage cross-current extraction to investigate the accumulation of VFAs in the studied solvents.

2. Experimental and analysis

2.1. Chemicals

Acetic acid (HAc, >99.7%), lactic acid (HLa, Ph.Eur.), propionic acid (HPr, >99.5%), butyric acid (HBu, >99%), nitric acid (1 M), n-octanol (>99%), trioctylamine (TOA, 98%), potassium chloride (>99%), anhydrous sodium phosphate dibasic (>99%), and anhydrous sodium sulfate (>99%) were purchased from Sigma-Aldrich. Hydrochloric acid (1 M) and potassium hydroxide (1 M) were supplied by Merck. [P_{666,14}][Cl] (Cyphos[®] IL101, >95%), [P_{666,14}][Br] (Cyphos[®] IL102, >95%), [P_{666,14}][Phos] (Cyphos[®] IL104, >95%), and [P_{666,14}][N(CN)₂] (Cyphos[®] IL105, >95%) were purchased from io-li-tec.

2.2. Artificial fermented wastewaters and model solutions

The composition of the aqueous solutions used for this study is shown in Table 2. Solution 3 is considered as an artificial fermented

wastewater resembling an actual fermented wastewater. Solutions 1–2f are simpler model solutions prepared to study the effects of dissolved salts and pH on extraction of VFAs.

2.3. Solvents

The solvents used in this study include TOA – n-octanol solutions and several phosphonium ionic liquids, and are listed in Table 3.

2.4. Experimental procedures

2.4.1. Single-stage liquid–liquid extraction

Single-stage liquid–liquid extraction experiments were performed at the volumetric solvent to feed ratio (S/F) of 3/5 using 3 mL of a solvent (see Table 3) and 5 mL of an aqueous model solution (see Table 2) at room temperature (20 ± 1 °C). The S/F of 3/5 was chosen to follow a certain experimental procedure described elsewhere [26]. To reach equilibrium, the liquid mixtures were magnetically stirred (>500 rpm) for 1 h. The time to reach equilibrium was experimentally validated to be less than 1 h for all feed – solvent pairs. After 1 h of stirring, phases were separated by a centrifuge (8000 rpm for 5 min). The phases were then sampled for analysis.

2.4.2. Multi-stage cross-current liquid–liquid extraction

Multi-stage cross-current liquid–liquid extraction experiments were carried out with solution 3 to monitor the accumulation of VFAs in the solvents in the presence of dissolved salts. After every extraction stage which was carried out in an identical way to the procedure described for single-stage extraction, the solvent phase was separated from the raffinate phase, and without any further treatment, it was contacted with fresh solution 3. Subsequent extraction stages were performed until the raffinate composition did not change anymore. The VFA loading of the VFA-saturated

Table 1
Typical composition of fermented wastewater.

Component	Chemical formula	Concentration (g/L)	pK _a
Acetic acid	CH ₃ COOH	2.5–10	4.76
Propionic acid	CH ₃ CH ₂ COOH	2.5–10	4.88
Butyric acid	CH ₃ (CH ₂) ₂ COOH	2.5–10	4.82
Lactic acid	CH ₃ CH(OH)COOH	2.5–10	3.86
Sodium	Na ⁺	1–5	
Potassium	K ⁺	1–5	
Chloride	Cl ⁻	1–10	
Phosphate	H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	1–10	
Sulfate	SO ₄ ²⁻	1–10	
Sulfide	S ²⁻	0.3	
Magnesium	Mg ²⁺	0.3	
Calcium	Ca ²⁺	0.3	
Ammonium	NH ₄ ⁺	0.1	
Trace elements (e.g. cobalt, nickel and iron)	Co, Fe, Ni (ionic forms)	10 ⁻⁴	
Inert COD (e.g. humic acid and fulvic acid)		1	
Microbes			

Table 2
Composition of applied model aqueous solutions.

Solution	Concentration (mol/L)									pH
	HAc	HPr	HBu	HLa	KCl	Na ₂ SO ₄	Na ₂ HPO ₄	HCl	HNO ₃	
1	0.17 (1 wt%)									2.8
1a	0.17				0.05					2.9
1b	0.17					0.05				3.0
1c	0.17						0.1			4.6
2	0.17						0.2			6.0
2a	0.17						0.2	0.01		5.9
2b	0.17						0.2	0.1		4.8
2c	0.17						0.2	1		0.4
2d	0.17						0.2		0.01	5.9
2e	0.17						0.2		0.1	4.8
2f	0.17						0.2		1	0.4
3	0.04 (0.25 wt%)	0.03 (0.25 wt%)	0.03 (0.25 wt%)	0.03 (0.25 wt%)	0.05	0.05	0.1			5.0

Table 3
Solvents used in this study and their water uptake as reported in the literature.

Solvent	Water uptake (wt% of solvent phase after extraction)
n-Octanol	4.9 [24]
10–50 wt% TOA in n-octanol	NA ^a
[P _{666,14}][Cl]	13.4 [25]–14.4 [21]
[P _{666,14}][Br]	6.3 [25]
[P _{666,14}][Phos]	14.4 [21]–16.0 [25]
[P _{666,14}][N(CN) ₂]	3.3 [21]

^a Not available.

solvents was measured after washing the solvent phases with KOH (1 M) and analyzing the alkaline phase with HPLC.

2.5. Analysis

The concentrations of HAc, HLa, HPr, HBu, H₃PO₄/H₂PO₄⁻/HPO₄²⁻/PO₄³⁻, [Phos]⁻ ([C₁₆H₃₄O₂P]⁻), and the summation of Cl⁻ and SO₄²⁻ concentrations were measured with HPLC [Agilent Hi-Plex H column (300 × 7.7 mm) and refractive index detector on a Agilent 1200 series HPLC system). Individual Cl⁻ and SO₄²⁻ concentrations and [N(CN)₂]⁻ and Br⁻ concentrations were quantified with IC (Metrosep A Supp 4–250/4.0 column and Metrohm 732 IC detector on a Metrohm 733 IC Separation Center). The water content was measured with Karl-Fischer titration (Metrohm 787 KF Titran). Na⁺ and K⁺ concentrations were measured with a flame photometer (BWB Flame Photometer XP). The pH was measured with a Metrohm pH probe (6.0234.100) connected to a Metrohm 780 pH meter.

3. Results and discussion

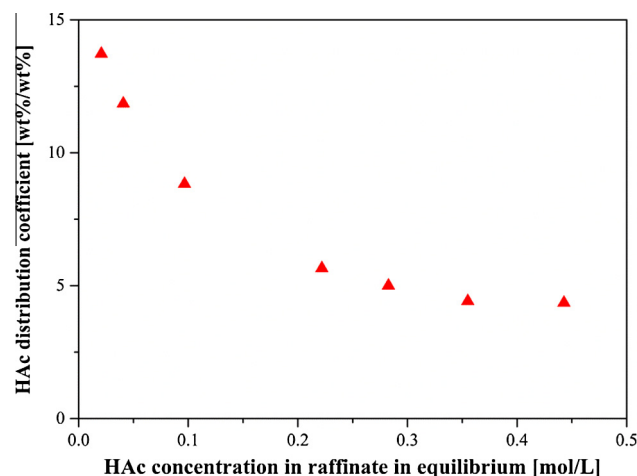
3.1. Single-stage HAc extraction from idealized solutions containing only water and acid

Various solvents have been reported for extraction of carboxylic acids from idealized aqueous solutions of only acid in water [18,22,27]. In this study, validation of the applied experimental methods was done with an idealized aqueous solution containing 1 wt% HAc (solution **1** in Table 2). TOA was applied diluted in n-octanol in the range of 0–50 wt%, and the phosphonium ionic liquids were used in their pure forms. The HAc distribution coefficients and water uptakes obtained after these experiments (with a single volumetric S/F ratio of 3/5) are summarized in Table 4.

Table 4 shows that the HAc distribution coefficient obtained with pure n-octanol is 0.6 which is perfectly in line with the values reported previously [14,28]. Table 4 also shows that the HAc

Table 4
Distribution coefficients and water uptakes for HAc extraction from solution **1** (pH_{initial} = 2.8, volumetric S/F = 3/5, T = 20 ± 1 °C).

Solvent	D _{HAc} (wt%/wt%)	Water uptake (wt% of solvent phase after extraction)
n-Octanol	0.6	4.8
10 wt% TOA in n-octanol	4.3	4.5
20 wt% TOA in n-octanol	8.8	3.7
30 wt% TOA in n-octanol	11.5	3.2
40 wt% TOA in n-octanol	9.9	2.5
50 wt% TOA in n-octanol	8.2	2.1
[P _{666,14}][Cl]	3.7	13.6
[P _{666,14}][Br]	2.2	6.6
[P _{666,14}][Phos]	17.0	14.1
[P _{666,14}][N(CN) ₂]	1.8	3.9

**Fig. 1.** HAc distribution coefficient as a function of HAc equilibrium concentration in raffinate phase (volumetric S/F = 3/5, T = 20 ± 1 °C).

distribution coefficients of TOA – n-octanol solutions follow a trend in which the highest values are obtained for the TOA concentration range of 20–40 wt%. This trend was reported previously for extraction of HLa with TOA – n-octanol solutions [16–18], and it was attributed to the stabilizing effect induced by n-octanol molecules on HLa – TOA complexes via hydrogen bonding [18]. By comparing the values presented in Table 4, it can be clearly seen that, at the low HAc concentration applied, [P_{666,14}][Phos] has a significantly higher HAc distribution coefficient than the other solvents. This is in line with the observation by Marták and Schlosser where it was shown that the HLa distribution coefficient of [P_{666,14}][Phos] strongly increases with decreasing raffinate concentration [21].

Table 5a

Total initial and final amounts of salt-originating anions for extractions from solutions **1a** (HAc + KCl, $pH_{\text{initial}} = 2.9$), **1b** (HAc + Na_2SO_4 , $pH_{\text{initial}} = 3.0$) and **1c** (HAc + Na_2HPO_4 , $pH_{\text{initial}} = 4.6$) at volumetric S/F of 3/5 and 20 ± 1 °C. The reported values for Ac^- , SO_4^{2-} and HPO_4^{2-} are the summation of all occurring forms.

Exp. No.		Initial mass in aqueous phase (g)					Final mass in aqueous phase (g)					Initial mass in solvent phase (g)					Final mass in solvent phase (g)					D_{HAc} (wt%/wt%)
		Ac^-	Cl^-	SO_4^{2-}	HPO_4^{2-}	Br^-	Ac^-	Cl^-	SO_4^{2-}	HPO_4^{2-}	Br^-	Ac^-	Cl^-	SO_4^{2-}	HPO_4^{2-}	Br^-	Ac^-	Cl^-	SO_4^{2-}	HPO_4^{2-}	Br^-	
	<i>20 wt% TOA in n-octanol</i>																					
1	Solution 1	0.106					0.018									0.088						8.8
2	Solution 1a	0.099	0.018				0.034	0.002								0.065	0.016					3.5
3	Solution 1b	0.098		0.044			0.046		0.015							0.052		0.029				2.1
4	Solution 1c	0.106			0.095		0.062			0.088						0.044			0.006			1.3
	<i>[P_{666,14}][Cl]</i>																					
5	Solution 1	0.106					0.031	0.025				0.348				0.075	0.324					3.7
6	Solution 1a	0.099	0.017				0.030	0.042				0.351				0.069	0.326					3.5
7	Solution 1b	0.103		0.046			0.033	0.048	0.013			0.344				0.070	0.296	0.033				3.5
8	Solution 1c	0.108			0.096		0.035	0.041		0.088		0.344				0.073	0.303		0.009			3.4
	<i>[P_{666,14}][Br]</i>																					
9	Solution 1	0.108					0.049							0.029		0.724	0.059				0.696	2.2
10	Solution 1a	0.098	0.017				0.046	0.009		0.049				0.049		0.717	0.052	0.008			0.668	2.0
11	Solution 1b	0.102		0.046			0.048		0.039	0.063				0.063		0.723	0.054		0.007		0.660	2.1
12	Solution 1c	0.108			0.096		0.063			0.095	0.051			0.051		0.717	0.046		0.001	0.666		1.4
	<i>[P_{666,14}][Phos]^a</i>																					
13	Solution 1	0.108					0.009									0.099						17.0
14	Solution 1a	0.100	0.018				0.032	0.001								0.068	0.017					3.3
15	Solution 1b	0.100		0.044			0.037		0.018							0.063		0.025				2.6
16	Solution 1c	0.107			0.095		0.061			0.086						0.046			0.009			1.2
	<i>[P_{666,14}][N(CN)₂]^b</i>																					
17	Solution 1	0.106					0.053									0.053						1.8
18	Solution 1a	0.099	0.018				0.049	0.014								0.050	0.004					1.7
19	Solution 1b	0.099		0.044			0.049		0.043							0.050		0.001				1.7
20	Solution 1c	0.107			0.095		0.078			0.094						0.030			0.001			0.7

^a [P_{666,14}][Phos] has been reported to be very hydrophobic, [29] and therefore, its leaching into aqueous phase is negligible. This was confirmed by analysis of the raffinates with HPLC.

^b Analysis of the raffinates with IC showed no measurable leaching of [N(CN)₂]⁻.

Table 5b

Initial and final amounts of salt-originating cations and water for extractions from solutions **1a** (HAc + KCl, $\text{pH}_{\text{initial}} = 2.8$), **1b** (HAc + Na_2SO_4 , $\text{pH}_{\text{initial}} = 3.0$) and **1c** (HAc + Na_2HPO_4 , $\text{pH}_{\text{initial}} = 4.8$) at volumetric S/F of 3/5 and 20 ± 1 °C.

Exp. No.		Initial mass in aqueous phase (g)			Final mass in aqueous phase (g)			Initial mass in solvent phase (g)			Final mass in solvent phase (g)		
		K ⁺	Na ⁺	Water	K ⁺	Na ⁺	Water	K ⁺	Na ⁺	Water	K ⁺	Na ⁺	Water
	<i>20 wt% TOA in n-octanol</i>												
1	Solution 1			9.974			9.775						0.199
2	Solution 1a	0.019		9.993	0.019		9.797						0.196
3	Solution 1b		0.021	9.978		0.021	9.782						0.195
4	Solution 1c		0.045	9.929		0.047	9.733						0.196
	<i>[P_{666,14}][Cl]</i>												
5	Solution 1			9.924			9.122						0.803
6	Solution 1a	0.019		9.934	0.019		9.125						0.809
7	Solution 1b		0.022	10.39		0.022	9.598						0.793
8	Solution 1c		0.046	10.08		0.047	9.282						0.793
	<i>[P_{666,14}][Br]</i>												
9	Solution 1			10.13			9.771						0.361
10	Solution 1a	0.019		9.904	0.019		9.547						0.358
11	Solution 1b		0.022	10.36		0.022	10.002						0.360
12	Solution 1c		0.046	10.12		0.049	9.757						0.358
	<i>[P_{666,14}][Phos]</i>												
13	Solution 1			10.12			9.289						0.834
14	Solution 1a	0.020		10.06	0.019		9.225						0.837
15	Solution 1b		0.021	9.987		0.022	9.153						0.834
16	Solution 1c		0.046	9.988		0.048	9.152						0.835
	<i>[P_{666,14}][N(CN)₂]</i>												
17	Solution 1			9.974			9.761						0.213
18	Solution 1a	0.019		9.954	0.019		9.725						0.228
19	Solution 1b		0.021	10.01		0.022	9.783						0.224
20	Solution 1c		0.045	9.948		0.047	9.745						0.204

To validate this trend, several HAc extraction experiments were performed with varying the initial HAc concentration in the aqueous phase while using the same volumetric S/F used for the rest of this study (3/5). The results are displayed in Fig. 1.

The water uptake of $[\text{P}_{666,14}][\text{Phos}]$ was remarkably high, but in line with the observations by others [21,25]. With the results of the idealized HAc solution being well in line with the values reported in the literature, the effects of salt-originating ions on extraction of VFAs can be discussed next.

3.2. Effects of dissolved salts on extraction of HAc

Each of the salts commonly present in fermented wastewater was separately added to a simple aqueous solution containing only HAc to prepare solutions **1a**, **1b** and **1c** (see Table 2). The effects of the salts on extraction of HAc were studied by comparison with HAc extraction from solution **1**, and in addition, the distribution of each salt-originating ion was studied. The obtained results for the anions are summarized in Table 5a, and the cation distributions are presented in Table 5b as well as water distribution. For the species Ac^- , SO_4^{2-} and HPO_4^{2-} , the reported values in Table 5a are the summation of all occurring forms (e.g. HAc and acetate anion in the case of Ac^-). Measuring the total aqueous concentrations and the water distribution over the phases enabled determination of the total amounts in the aqueous raffinates and in the extract phases. The values presented in Tables 5a and 5b were obtained from extraction systems composed of 10 g of solution **1**, **1a**, **1b** or **1c** and a solvent at a volumetric S/F of 3/5.

As can be seen in the first section of Table 5a, for all of the extraction experiments with 20 wt% TOA in n-octanol where Cl^- , SO_4^{2-} or HPO_4^{2-} was present, a reduced distribution of Ac^- was observed. Although the initial pH of solution **1a** was almost the same as that of solution **1** (see Table 2), almost all the Cl^- , initially present in solution **1a**, was co-extracted along with Ac^- . Since no cation was extracted by 20 wt% TOA in n-octanol (see Table 5b),

Cl^- has to be extracted along with H^+ to maintain the charge neutrality in the solvent phase. Based on the extraction mechanisms proposed for similar cases in the literature [30,31], and the fact that Cl^- and H^+ do not form molecular HCl in aqueous phase, TOA most likely forms complexes with H^+ at the interface between the aqueous and organic phases which is then followed by extraction of Cl^- as the counter-ion forming $[\text{TOAH}][\text{Cl}]$ in the solvent phase. This extraction mechanism is favored for extraction of strong acids (HCl here), whereas weak acids (HAc here) may distribute over the phases in their undissociated forms [32]. The same phenomenon was observed when 20 wt% TOA in n-octanol was used to extract HAc from solutions **1b** and **1c**. Here, the net extracted species were H_2SO_4 and H_3PO_4 . In the case of solution **1c**, the higher pH caused by the presence of HPO_4^{2-} resulted in the lack of H^+ needed for extraction of HAc and H_3PO_4 .

Table 5a shows that, when $[\text{P}_{666,14}][\text{Cl}]$ was used as the solvent, next to extraction of Ac^- , some SO_4^{2-} and HPO_4^{2-} (to a lower extent) was also extracted. This in combination with the significant leaching of Cl^- from $[\text{P}_{666,14}][\text{Cl}]$ phase into aqueous phase (7–14% of the initial Cl^- content in $[\text{P}_{666,14}][\text{Cl}]$, depending on the model solution used) suggests that ion exchange was one of the extraction mechanisms. Similar to Cl^- , Br^- also significantly leached from $[\text{P}_{666,14}][\text{Br}]$ phase into the aqueous phases resulting in a Br^- content loss of 4–9% from the solvent phase, depending on the model solution used. The Cl^- and Br^- leaching from the $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{Br}]$ phases indicates that one of the HAc extraction mechanisms used by these two ionic liquids is ion exchange through which Cl^- or Br^- are replaced with Ac^- . The ion exchange mechanism in these cases is an irreversible interaction, as without replacing leached Cl^- and Br^- , recovery of extracted Ac^- from $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{Br}]$ phases is impossible. To further support the presence of ion exchange mechanism in the case of $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{Br}]$, the pH of all the obtained raffinates was also measured. The measured values are presented in Table 6 and compared with the pH of their associated model solutions.

Table 6
Equilibrium pH of obtained raffinates after extraction compared with that of their associated model solutions.

Exp. No.	Initial pH of model solution	Equilibrium pH of raffinate
<i>20 wt% TOA in n-octanol</i>		
1	Solution 1	2.8
2	Solution 1a	2.9
3	Solution 1b	3.0
4	Solution 1c	4.6
<i>[P_{666,14}][Cl]</i>		
5	Solution 1	2.8
6	Solution 1a	2.9
7	Solution 1b	3.0
8	Solution 1c	4.6
<i>[P_{666,14}][Br]</i>		
9	Solution 1	2.8
10	Solution 1a	2.9
11	Solution 1b	3.0
12	Solution 1c	4.6
<i>[P_{666,14}][Phos]</i>		
13	Solution 1	2.8
14	Solution 1a	2.9
15	Solution 1b	3.0
16	Solution 1c	4.6
<i>[P_{666,14}][N(CN)₂]</i>		
17	Solution 1	2.8
18	Solution 1a	2.9
19	Solution 1b	3.0
20	Solution 1c	4.6

As can be seen in Table 6, the pH of the raffinates obtained after extraction with [P_{666,14}][Cl] or [P_{666,14}][Br] is lower than that of their associated model solutions. This is due to the replacement of Ac⁻ with Cl⁻ or Br⁻ in the aqueous phases as a result of ion exchange mechanism. Since HCl and HBr completely dissociate in an aqueous phase contrary to the weak acid HAc, the removal of Ac⁻ has resulted in an increased H⁺ concentration. Ion exchange was responsible for 55% or 35% of the removal of Ac⁻ from solution **1** using [P_{666,14}][Cl] or [P_{666,14}][Br] respectively. The rest was due to extraction of molecular HAc. Extraction of molecular HAc into these ionic liquids was promoted by hydrogen bonding between the proton of HAc and a hydrogen bond donating atom (Cl⁻, Br⁻ and/or oxygen of exchanged Ac⁻). The lower water uptake of [P_{666,14}][Br] compared to that of [P_{666,14}][Cl] shows its weaker tendency toward hydrogen bonding which may explain the slightly lower HAc extraction capacity of [P_{666,14}][Br]. The significant hydrophilicity of [Cl]⁻ and [Br]⁻ makes [P_{666,14}][Cl] and [P_{666,14}][Br] too instable, as was shown by their significant leaching. Therefore, these ionic liquids are not promising solvents for extraction of VFAs from aqueous solutions.

Table 5a shows that [P_{666,14}][Phos] extracted significant amounts of Ac⁻, Cl⁻, SO₄²⁻ and HPO₄²⁻. It was also observed that [Phos]⁻ was highly stable in the [P_{666,14}][Phos] phases. Furthermore, [P_{666,14}][Phos] did not extract any Na⁺ or K⁺ (see Table 5b). These imply that, in terms of extraction mechanism, [P_{666,14}][Phos] is similar to 20 wt% TOA in n-octanol, i.e. mineral acids are extracted via interfacial protonation of the extractant followed by extraction of their anions to maintain charge balance. In this case, the anion of [P_{666,14}][Phos] is protonated, and due to the hydrophobic character of [Phos], it remains in the ionic liquid phase in protonated form as well.

[P_{666,14}][N(CN)₂] seems not to be affected by any of the salt-originating anions (see Table 5a), as it did not extract any considerable amount of any of them while keeping a constant extraction capacity for HAc when it was exposed to solutions **1**, **1a** and **1b**. It did not extract any Na⁺ or K⁺ either (see Table 5b). The reduction in its HAc extraction capacity while being exposed to solution **1c** was due to the higher pH of solution **1c** which reduced the amount of molecular HAc (extracted species) in the aqueous phase. Based on this observation, it may be concluded that interfacial protonation of Ac⁻ did not take place, and extraction of HAc was mainly through hydrogen bonding of the molecular form of the acid.

Contrary to [P_{666,14}][Cl] and [P_{666,14}][Br], [P_{666,14}][Phos] and [P_{666,14}][N(CN)₂] were found to be highly stable, and no measurable leaching of [Phos]⁻ or [N(CN)₂]⁻ was detected in the aqueous phases.

From the results presented in Tables 5a and 5b, it can be concluded that multiple phenomena such as co-extraction of mineral acids, ion exchange, and extraction through intermolecular interactions (e.g. hydrogen bonding) affect HAc distribution. However, the role of pH in the observed changes in HAc distribution was not clear enough based on the experiments described in this section. pH is often a very important factor in liquid–liquid extraction and therefore, to clarify its effect on HAc extraction, additional experiments (next subsection) were carried out.

3.3. Effect of pH on extraction of HAc

The effect of pH was studied by adding strong acids to solution **2**. The obtained solutions were named solutions **2a**, **2b**, **2c**, **2d**, **2e** and **2f** (see Table 2). Fig. 2 shows the HAc distribution coefficients obtained after the extraction experiments performed with [P_{666,14}][Phos] and [P_{666,14}][N(CN)₂].

As can be seen in Fig. 2, decreasing the pH of the aqueous solution has resulted in increase in the HAc distribution coefficient of both of the solvents. This confirms the nature of the extraction mechanism described in the previous section, proceeding through hydrogen bonding of molecular HAc and not ion exchange of acetate anion. By lowering pH, the dissociation equilibrium of HAc in

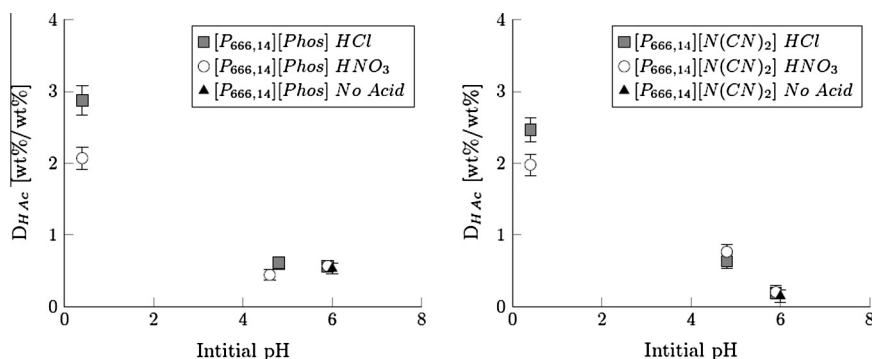


Fig. 2. HAc distribution coefficient of [P_{666,14}][Phos] and [P_{666,14}][N(CN)₂] using solutions **2a**, **2b**, **2c**, **2d**, **2e** and **2f** (volumetric S/F = 3/5, T = 20 ± 1 °C).

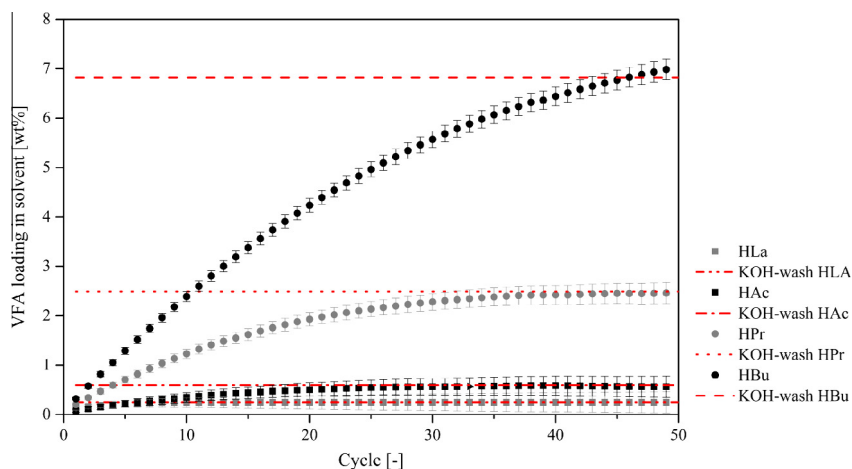


Fig. 3a. Multiple extraction stages using solution **3** and $[P_{666,14}][Phos]$. Points correspond to VFA loadings determined by analysis of aqueous raffines. Dashed lines correspond to maximum concentrations obtained from base wash of solvent phase at the end of cross current extraction series.

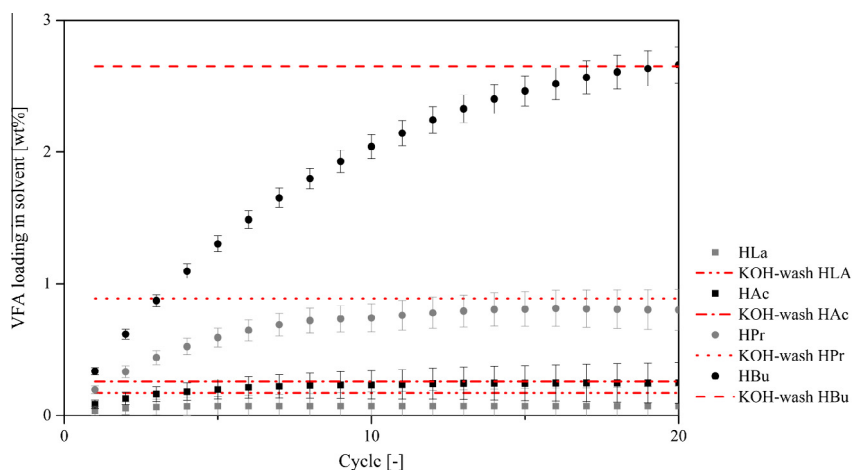


Fig. 3b. Multiple extraction stages using solution **3** and 20 wt% TOA in n-octanol. Points correspond to VFA loadings determined by analysis of aqueous raffines. Dashed lines correspond to maximum concentrations obtained from base wash of solvent phase at the end of cross current extraction series.

the aqueous phase shifts to HAc being the predominant form present, and therefore, the ongoing equilibria series (dissociation, partitioning and organic phase complexation) shifts to a higher HAc distribution. This was previously observed when amines and fatty acids were used as solvents [14,33]. Compared to the HAc distribution observed for $[P_{666,14}][Phos]$ using solution **1** (see Fig. 1), the maximum HAc distribution obtained for $[P_{666,14}][Phos]$ in the presence of strong acids, as seen in Fig. 2, is much lower. When a strong acid is present, $[P_{666,14}][Phos]$ co-extracts the anion of the strong acid (here Cl^- or NO_3^-) together with H^+ in significant amounts which results in a significantly reduced solvent capacity for HAc.

3.4. Liquid–liquid extraction – multi-stage

From the previous subsections, it was concluded that the salts present in fermented wastewater may significantly reduce the HAc distribution of the solvent. However, since all the results presented so far were obtained from single-stage extraction experiments, they do not elucidate any maximum solvent capacity obtained when the solvent is in equilibrium with fermented wastewater. In order to determine the maximum VFA loading of the solvents $[P_{666,14}][Phos]$ and 20 wt% TOA in n-octanol (benchmark solvent in many studies and second best in HAc extraction after $[P_{666,14}][Phos]$) when they are in equilibrium with the

artificial fermented wastewater (solution **3**), two series of cross-current extraction experiments were carried out according to the method described in Section 2.4.2. Figs. 3a and 3b show the gradual increase in the VFA content of the solvents with increasing the number of extraction stages. The points in Figs. 3a and 3b correspond to the VFA loadings determined by calculating the amount of VFA extracted based on the change in the aqueous phase concentration after every extraction stage, whereas the dashed lines correspond to the maximum VFA loadings determined by washing the solvent phases with KOH (1 M) which allowed a complete recovery of extracted VFAs from the solvents. As can be seen in Figs. 3a and 3b, “KOH-wash” lines are in good agreement with the maximum loadings determined by analysis of raffines presented by the points.

As can be seen in Figs. 3a and 3b, both of the solvents show the same order in VFA extraction efficiency: $W_{HLA} < W_{HAc} < W_{HPr} < W_{HBu}$. This trend is logical, as with similar pK_a s and increasing the number of carbons, the growing hydrophobic domain in acid leads to a better extraction. HLa is a C_3 -acid, but due to its additional $-OH$ functionality and lower pK_a , it was the most challenging VFA to extract.

Table 7 shows the VFA loadings and water contents of the solvents in equilibrium with solution **3**. The VFA loading values correspond to the KOH-wash lines presented in Figs. 3a and 3b. Table 7 also shows the VFA and water content of the recovered VFA-water

Table 7

Maximum VFA loadings in solvents in equilibrium with solution **3** ($C_{\text{HLA}} = C_{\text{HAc}} = C_{\text{HPr}} = C_{\text{HBu}} = 0.25$ wt%, pH = 5.0).

	[P _{666,14}][Phos]		20 wt% TOA in n-octanol	
	Loading in solvent phase (wt%)	Concentration in recovered stream (wt%)	Loading in solvent phase (wt%)	Concentration in recovered stream (wt%)
HLA	0.25	1.6	0.17	2.2
HAc	0.60	3.7	0.26	3.3
HPr	2.49	15.4	0.89	11.2
HBu	6.82	42.2	2.65	33.5
Water	5.99	37.1	3.95	50.0

streams from the solvents assuming a complete recovery of VFAs from the solvents is possible with no addition of any extra water or chemical. This assumption is not so unrealistic, as in the literature, it has been reported that under deep vacuum and high temperatures, extracted organic acids can be recovered from extracting solvents [34]. Such a method for recovery of extracted VFAs is advantageous over any form of back-extraction, as the resulting VFA concentrations will be much higher in the obtained stream, as compared to those achieved by back-extraction. Furthermore, the VFAs will not be contaminated by salts, as would be the case in a back-extraction using an alkaline solution.

As can be seen in Table 7, the water content of [P_{666,14}][Phos] has decreased with increasing its VFA loading. This phenomenon has been previously observed and reported by Schlosser et al. [21,29] Table 7 shows that if the assumption made above holds, starting with a combined VFA concentration of 1 wt% in solution **3**, a final combined VFA concentration of up to ~ 65 wt% can be obtained. It must be noted that since [P_{666,14}][Phos] has higher VFA loadings than 20 wt% TOA in n-octanol does, it will deliver the recovered stream at a lower S/F.

4. Conclusions

In fermented wastewater, significant amounts of dissolved salts accompany VFAs. This makes fermented wastewater a complex aqueous solution containing many ions. In this study, the effects of these ions on extraction of VFAs from fermented wastewater was studied using several simpler aqueous model solutions each containing HAc and a single salt. It was observed that the cations originating from these salts (Na⁺ and K⁺) are not extracted at all. On the other hand, the anions were co-extracted which resulted in significant reduction in the VFA extraction capacity of the solvents. Also, some salts increased the pH of the aqueous solutions, thereby reducing VFA distribution. [P_{666,14}][Phos] was found to be the solvent with the highest extraction capacity for VFAs. Through multi-stage cross-current extraction, [P_{666,14}][Phos] achieved a maximum combined VFA loading of up to 10 wt% in

equilibrium with solution **3**, the solution resembling an actual fermented wastewater (containing 0.25 wt% of each VFA).

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