

## CO<sub>2</sub>-enhanced extraction of acetic acid from fermented wastewater

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### Supporting information

#### 1. Atmospheric extraction data

The data reported in the Table S2 is obtained from a single-stage extraction system consisting of approximately 10 g of an aqueous solution and approximately 5 g of a solvent to achieve a volumetric S/F of 3/5 which is used for all the experiments reported in this article. The aqueous phases were prepared based on the most simple fermented wastewater model solution used in this article, pH 2.8 solution, to better understand the phenomenon associated with every single dissolved salt present in an actual fermented wastewater. The initial composition of the aqueous solutions is brought in the following Table S1:

**Table S1:** Initial composition of aqueous solutions prepared to study effects of salt-originated ions and pH on extraction of acetic acid

Solution	Concentration [mol/L]				pH
	HAc	KCl	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	
1	0.17 (1 wt%)				2.8
1a	0.17	0.05			2.8
1b	0.17		0.05		3.0
1c	0.17			0.1	4.8

**Table S2:** Initial and final distribution of salt-originated ions and water in aqueous and solvent phases using aqueous solutions presented in Table S1

	$M_{aq,i}^a$ [g]							$M_{aq,f}^b$ [g]							$M_{s,f}^c$ [g]								
	Ac <sup>d</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-d</sup>	HPO <sub>4</sub> <sup>2-d</sup>	Na <sup>+</sup>	K <sup>+</sup>	Water	Ac <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HPO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Water	Ac <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HPO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Water		
<b>20 wt% TOA in n-octanol</b>																							
Solution 1	0.106						9.974	0.018						9.775	0.088								0.199
Solution 1a	0.099	0.018				0.019	9.993	0.034	0.002				0.019	9.797	0.065	0.016							0.196
Solution 1b	0.098		0.044		0.021		9.978	0.046		0.015		0.021		9.782	0.052		0.029						0.195
Solution 1c	0.106			0.095	0.045		9.929	0.062			0.088	0.047		9.733	0.044			0.006					0.196
<b>[P<sub>666,14</sub>][Phos]</b>																							
Solution 1	0.108						10.122	0.009						9.289	0.099								0.834
Solution 1a	0.100	0.018				0.020	10.062	0.032	0.001				0.019	9.225	0.068	0.017							0.837
Solution 1b	0.100		0.044		0.021		9.987	0.037		0.018		0.022		9.153	0.063		0.025						0.834
Solution 1c	0.107			0.095	0.046		9.988	0.061			0.086	0.048		9.152	0.046			0.009					0.835

<sup>a</sup>: initial mass in aqueous phase

<sup>b</sup>: final mass in aqueous phase

<sup>c</sup>: final mass in solvent phase

<sup>d</sup>: these species are present in multiple forms, e.g. Ac<sup>-</sup> is present as acetate, but also as HAC

Table S3 compares the water uptake of the solvents after a single-stage extraction with pH 4.8 solution with the water uptakes of the acetic acid-water-saturated solvents after multi-stage cross-current extraction with pH 4.8 solution.

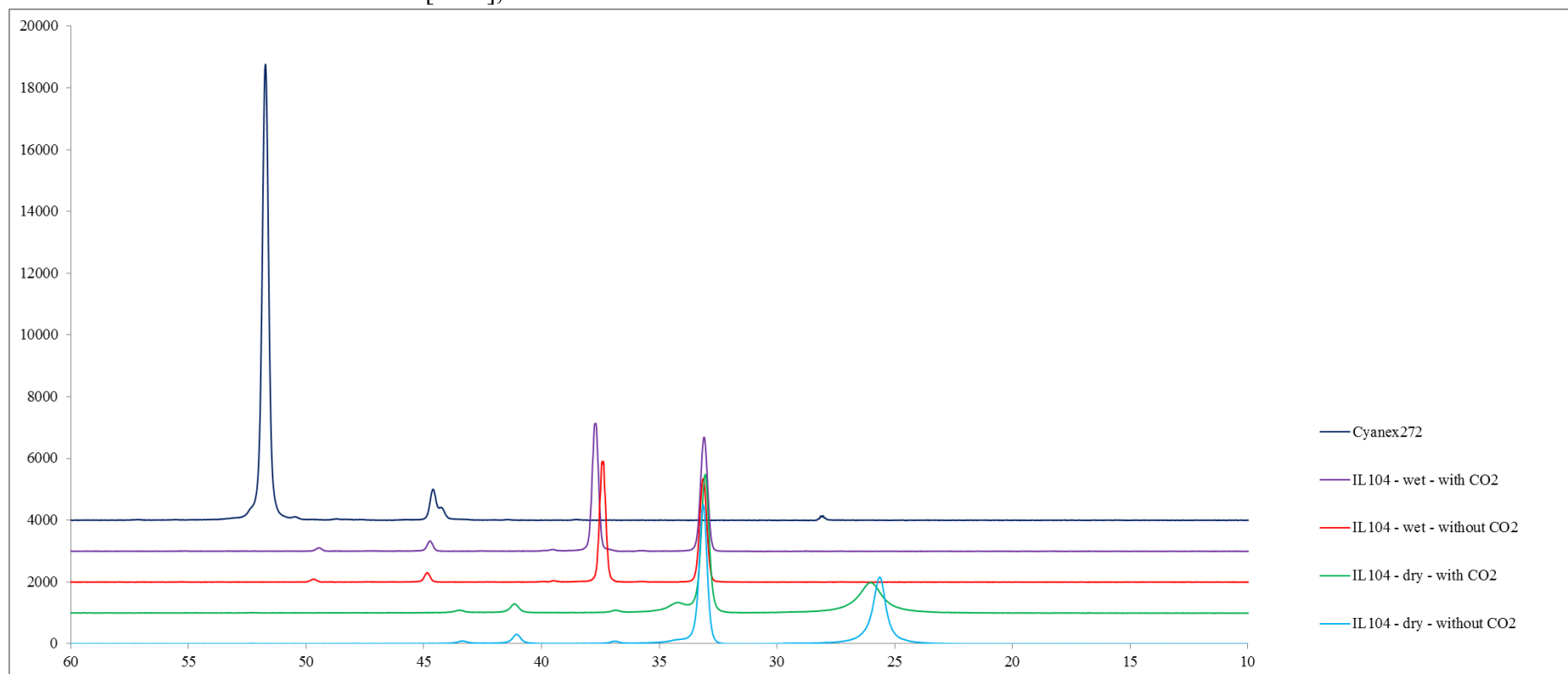
**Table S3:** Water uptake of solvents

Solvent	wt% water after single extraction	wt% water after cross-current extraction
[P <sub>666,14</sub> ][Phos]	15.7	8.4
20 wt% TOA in octanol	3.7	3.7

## 2. Extractions under CO<sub>2</sub>-pressure

To get more insights in the interaction between the ionic liquid [P<sub>666,14</sub>][Phos] and CO<sub>2</sub>, the IL was studied by <sup>31</sup>P-NMR.

Figure S1: <sup>31</sup>P-NMR spectra of [P<sub>666,14</sub>][Phos] (which is IL-104) under various conditions, and of Cyanex272, which is the commercially available molecular form of the anion [Phos], thus HPhos.



The bottom spectrum of dry IL-104 in absence of CO<sub>2</sub> shows two main peaks, the phosphorus in the anion at 25.6 ppm, and the phosphorus in the cation at 33.0. The smaller signals are apparently some impurities, as the IL-104 is sold 95% pure. Going upwards through the spectra, the

second spectrum is from IL-104 that was bubbled with CO<sub>2</sub>, and that spectrum shows a bit broadened anion spectrum, but no significant changes. The third spectrum is wet IL-104, but without CO<sub>2</sub>, this spectrum shows a significant change as compared with the dry IL-104 and the dry IL-104 that is sparged with CO<sub>2</sub>. The anion peak is now at 37.4 ppm. Sparging this wet IL-104 with CO<sub>2</sub> does not significantly change the spectrum, although there is a very slight change in the chemical shift to 37.7 ppm. This significant change in the chemical shift of the anion is due to the changed environment, as it is known from the work by Blahusiak and Schlosser that aggregates of water are formed in IL-104. To confirm that it is not the molecular form of the anion, diisooctylphosphinic acid (Cyanex 272 in the figure, the commercial name), that is causing this signal, this species was also analyzed by <sup>31</sup>P-NMR and presented as the top spectrum, showing a signal at 51.7ppm.