Reactive extraction of 3-hydroxypropionic acid using tertiary and quaternary amines in decanol and comparison with its isomer 2-hydroxypropionic (lactic) acid

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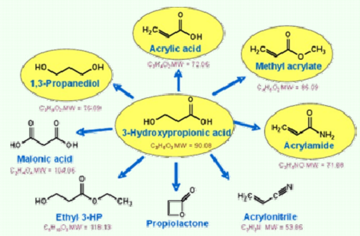
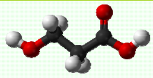
Context

- Within the framework of the development of the **bioeconomy**: → increasing drive towards the production of chemicals from renewable resources.
- Interest in the sustainable production at the industrial scale of bio-based polymer building blocks, such as the bifunctional **carboxylic acid 3-hydroxypropanoic acid** (3-HP), is growing [1].
- **Biotechnology** is believed to provide a sustainable route to produce 3-HP.



- **Solve product inhibition of 3-HP producing microorganisms**
- **Develop robust processes that integrate bioconversion and downstream processing**

Aims



- This work aims to:
  - **study** the **reactive extraction of 3-HP**, a potentially biocompatible technique that drew a lot of attention lately for the extraction of 2-hydroxypropionic (lactic) acid (**2-HP**)
  - **optimize** the **operating conditions**, bearing in mind the constrains associated with the **integrated process** of bioconversion and reactive extraction
  - better **understand** and **control** the **specific mechanisms** involved in reactive extraction prior to the implementation of the integrated process

Material & Methods

Reactive extraction theory

Tertiary amines R_3N

$$AH \leftrightarrow A^- + H^+$$
$$\overline{R_3N} + H^+ \leftrightarrow \overline{R_3NH^+}$$
$$\overline{R_3NH^+} + A^- \leftrightarrow \overline{R_3NHA}$$

Overall reaction: $\overline{R_3N} + HA \leftrightarrow \overline{R_3NHA}$

Quaternary amines R_4NX

$$AH \leftrightarrow A^- + H^+$$
$$\overline{R_4NX} \leftrightarrow \overline{R_4N^+} + \overline{X^-}$$

Overall reaction: $\overline{R_4NX} + A^- \leftrightarrow \overline{R_4NA} + X^-$

Basic principle: the extractant (amine diluted in the organic phase) selectively forms a complex with the organic acid (AH in the aqueous phase) [2].

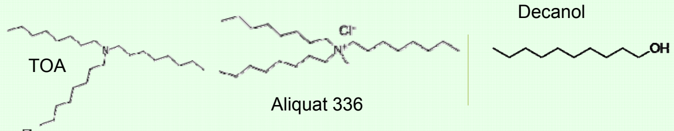
Aqueous phase

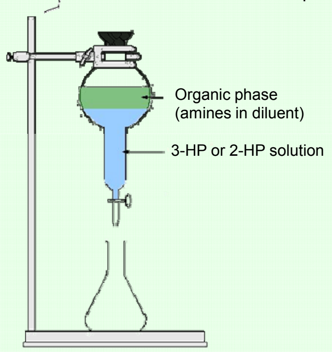
- 3-HP and 2-HP solutions of 1 $g.L^{-1}$. Natural pH of 3.2 and 2.9 respectively.
- The natural pH was adjusted with 12N HCl or 1N NaOH solutions when required.

Organic phase

- Extactants: Tri-*n*-otylamine (TOA) and tri-*n*-octylmethylammonium chloride (Aliquat 336), pure or a mixture of them. Concentrations of up to 60% vol/vol in diluent.
- Diluent: *n*-decanol.

Equilibrium tests in separatory funnels





***Operating conditions*:**

- T = 25°C
- Equilibrium time = 7 days
- Two extraction modes:
  - Static (non-dispersive)
  - Dynamic (dispersive shaking)

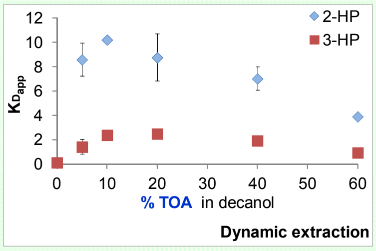
***Apparent distribution coefficient*:**

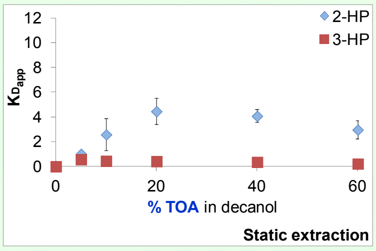
$$K_{D_{app}} = \frac{[HA]_{org} + [A^-]_{org}}{[HA]_{aq} + [A^-]_{aq}}$$

$[HA]_{aq}$ measured using HPLC

Results & Discussion

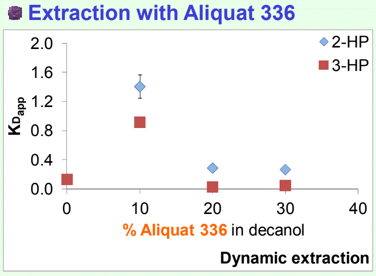
Extraction with TOA

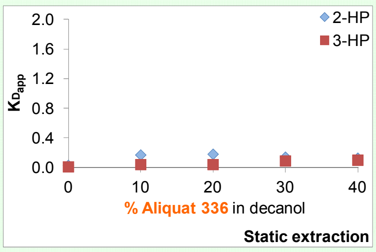




- 2HP extraction is more favored than 3HP, but similar behaviors are exhibited.
- Increasing TOA fraction up to 10-20% → enhanced $K_{D_{app}}$. Nevertheless, the solvation of the acid-amine complex is not favored for higher TOA fractions.
- For dynamic extraction: $K_{D_{app}}$ is improved thanks to the increase in interfacial area → overcomes the mass transfer limitation due to complex formation.

Extraction with Aliquat 336

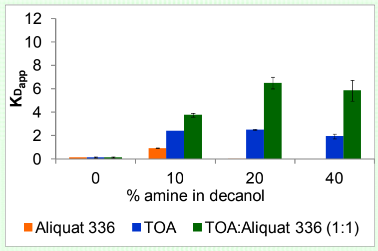




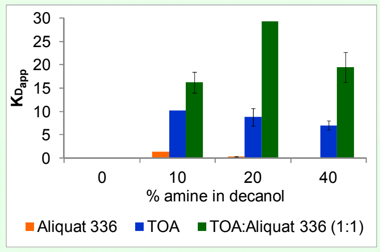
- Extraction by Aliquat 336 is not favored for both acids: the initial pH of the acids < pKa, while Aliquat 336 reacts with the dissociated forms of the acids.

Extraction with mixtures of TOA and Aliquat 336

Extraction of 3-HP

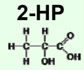
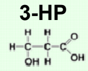


Extraction of 2-HP

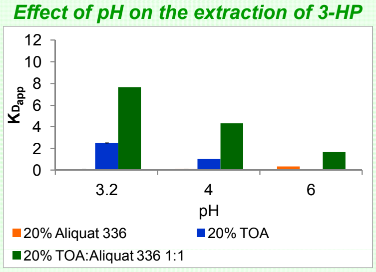


- **Synergy** between amines: $K_{D_{app}}$ obtained in the case of mixed extractants is higher than the sum of the $K_{D_{app}}$ of each extractant when used alone.
- As for individual amines, the higher affinity of 3-HP to water as compared to 2-HP and its higher pKa → huge difference between $K_{D_{app}}$ for 3-HP vs 2-HP.

Comparison of key properties

	2-HP	3-HP
		
pKa	3.86	4.51
Hydrophobicity ($Log\ K_{o/w}$)	-0.65	-0.89

Effect of pH on the extraction of 3-HP



- Mixed extractants give much higher $K_{D_{app}}$ at lower pH values → the presence of Aliquat 336 favors the 3-HP extraction by TOA[3].

Conclusion & Prospects

- 3-HP reactive extraction by a synergistic mixture of TOA and Aliquat 336 in *n*-decanol showed highly interesting performances over a wide range of pH values.
- The reactive extraction was shown to be predominantly controlled by interfacial chemical reactions. Performing it in a membrane contactor will optimize the process.
- Further work is needed to better understand the specific mechanisms of synergy between amines and optimize the reactive extraction of 3-HP.

[1] Van Maris AJA, Konings WN, van Dijken JP, Pronk JT. Metab. Eng. 6:245-255, 2004. [2] Kyuchoukov G, Yankov D. Ind. & Eng. Chem. Res. 51: 9117-9122, 2012. [3] Kyuchoukov, G., Marinova, M., Molinier, J., Albet, J. and Malmary, G. Ind. & Eng. Chem. Res. 40: 5623-5639, 2001.