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# 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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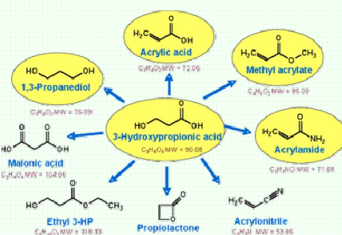
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## Context

- 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-hydroxypropionic 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

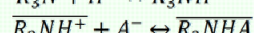
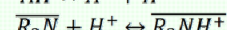
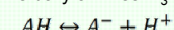
- This work aims to:

- 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 constraints 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

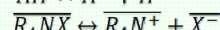
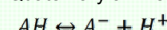
Tertiary amines  $R_3N$



Overall reaction:  $R_3N + HA \leftrightarrow R_3NHA$

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

Quaternary amines  $R_4NX$



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

### 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]<sub>aq</sub> measured using HPLC

### Aqueous phase

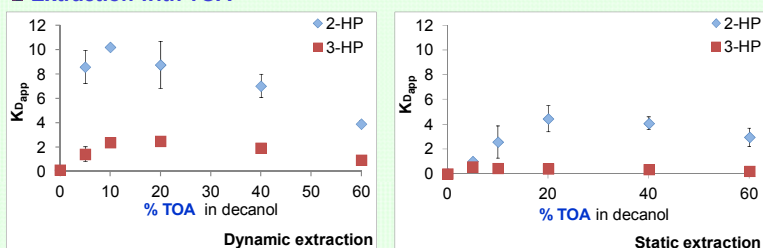
- 3-HP and 2-HP solutions of 1 g.L<sup>-1</sup>. Natural pH of 3.2 and 2.9 respectively.
- The natural pH was adjusted with 12N HCl or 1N NaOH solutions when required.

### Organic phase

- Extractants: Tri-*n*-octylamine (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.

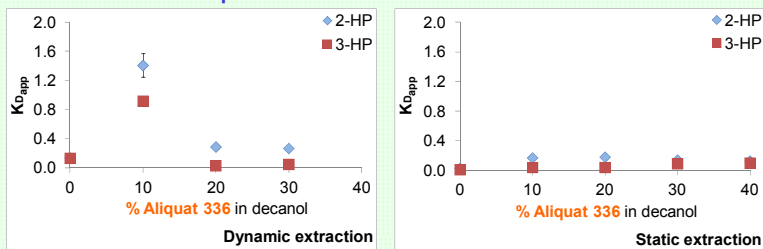
## Results & Discussion

### Extraction with TOA



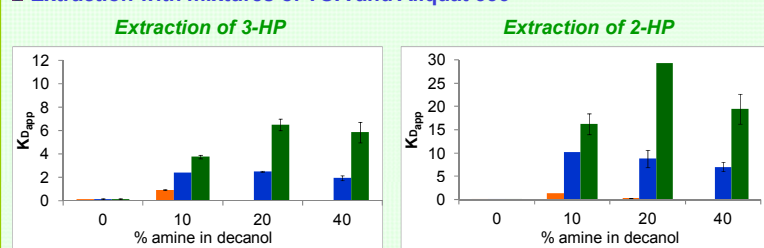
- 2HP extraction is more favored than 3HP, but similar behaviors are exhibited.
- Increasing TOA fraction up to 10-20% → enhanced  $K_{D,app}$ . Nevertheless, the solvation of the acid-amine complex is not favored for higher TOA fractions.
- For dynamic extraction:  $K_{D,app}$  is improved thanks to 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 < pK<sub>a</sub>, while Aliquat 336 reacts with the dissociated forms of the acids.

### Extraction with mixtures of TOA and Aliquat 336

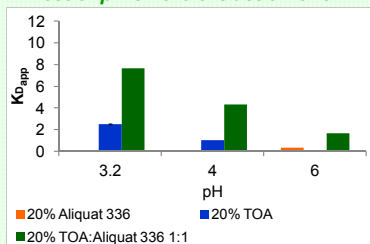


- Synergy** between amines:  $K_{D,app}$  obtained in the case of mixed extractants is higher than the sum of the  $K_{D,app}$  of each extractant when used alone.
- As for individual amines, the higher affinity of 3-HP to water as compared to 2-HP and its higher pK<sub>a</sub> → huge difference between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

### Comparison of key properties

	2-HP	3-HP
pK <sub>a</sub>	3.86	4.51
Hydrophobicity (Log K <sub>ow</sub> )	-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<sup>[3]</sup>.

## 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.