Potential of ionic liquids for VOC biodegradation in a two-liquid phase system

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Context

Hydrophobic VOC issues

- Absorption in an organic phase (solvent)
- VOC biodegradation
- Recycling of the solvent
Hydrophobic VOC (Toluene, dimethylsulfide, dimethyldisulfide)

TPPB for air treatment are based on the addition of a non-aqueous phase with high affinity for poorly water-soluble VOC.
Choice of the solvent

- Viscosity
- Absorption capacity and velocity
- Density
- Toxicity
- Partition coefficient (octanol/water) log P
- Cost effective

Silicone oils (like PDMS: PolyDiMethylsiloxane)

Ionic liquids
Choice of Ionic liquids (IL)

- No investigations on VOC affinity towards IL nor VOC biodegradation in the presence of IL.
- Possibility to fine-tune the IL physicochemical properties by modifying their chemical structure.
- IL tuning → overcome toxicity drawbacks → broaden application spectrum.
Ionic liquids (IL)

IL are organic salts existing as liquids below a threshold temperature (~100 °C). The most investigated IL are based on imidazolium salts.

1-Butyl-3-Methyl-Imidazolium hexafluorophosphate

[BMIM]$^+$
Ionic Liquids investigated

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Chemical structure</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butyl-3-methylimidazolium hexafluorophosphate</td>
<td>![Chemical structure](1-butyl-3-methylimidazolium hexafluorophosphate.png)</td>
<td>[BMIM][PF₆]</td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>![Chemical structure](1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.png)</td>
<td>[BMIM][NTF₂]</td>
</tr>
<tr>
<td>*tri(C₈C₁₀)methylammonium chloride *</td>
<td>![Chemical structure](tri(C₈C₁₀)methylammonium chloride.png)</td>
<td>Aliquat</td>
</tr>
</tbody>
</table>

* Mixture of R= C₈ and C₁₀, with C₈ predominating

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Chemistry and Process Engineering team

IL as green solvents

Green solvents

Ionic Liquids

- Negligible vapor pressure below 400 °C
- Non-flammable
- High thermostability

High IL affinity towards interesting molecules in biotechnology such as:
- Phenolic compounds
- Carbohydrates
- Organic acids
- Hydrocarbons

(Zhao et al. 2005)
Aim of this work

Evaluate the potential of these IL for TPPB construction. The evaluation was based on IL affinity, toxicity and biodegradability for three model VOC:

- Toluene
- Dimethylsulfide (DMS)
- Dimethyldisulfide (DMDS)
Experimental sequence

Step 1: IL Toxicity
   Glucose uptake inhibition

Step 2: IL Biodegradability
   BOD₅ and long term biodegradation tests

Step 3: Affinity for VOC
   Partition coefficient

Step 4: VOC Biodegradation
   Batch cultures

Biocatalyst: activated sludge

Chemistry and Process Engineering team
Material and Methods

**Glucose uptake inhibition**

- 120 mL glass bottles experiments
  - 2 mL activated sludge
  - 18 mL of mineral salt medium
  - Glucose (2 g L$^{-1}$) and IL (5 and 10% v/v).
  - 48 h, 30°C, 300rpm.

  (Baumann et al. 2005)

Enzymatic determination of the remaining glucose in the aqueous phase
Results - Toxicity

Toxicity

Glucose uptake inhibition

( ) [BMIM][PF$_6$], ( ) [BMIM][NTF$_2$], ( ) Aliquat and (Δ) control without IL

Similar uptake rate than controls after 24 h
Material and Methods

Biological Oxygen Demand experiments (BOD$_5$)

- Oxitop IS6 (WTW, Alès, France)
- Activated sludge

- where BOD$_5^{EB}$ is the BOD$_5$ value of the endogenous breath controls

$$\%\text{Biodegradation} = \frac{\text{BOD}_5 - \text{BOD}_5^{EB}}{\text{COD}} \times 100$$
Material and Methods

Long term biodegradation tests (LTB)

IL biodegradation was expressed as a percentage of IL uptake during 30 days of incubation at 30°C under magnetic agitation (300 rpm).
Initial IL concentration (10 g/L)

IL concentration in the aqueous phase was quantified by spectrophotometric measurements at 210 nm.

(Romero et al. 2008)
Results – IL biodegradability

Biodegradability

BOD$_5$ tests & LTB tests

LTB tests

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>BOD5 test</th>
<th>LTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][PF$_6$]</td>
<td>No (% Biodegradation ≈ 0%)</td>
<td>No</td>
</tr>
<tr>
<td>[BMIM][NTF$_2$]</td>
<td>No (% Biodegradation ≈ 0%)</td>
<td>No</td>
</tr>
</tbody>
</table>

Remaining IL (% initial)

- [C4MIM][NTF$_2$]
- [C4MIM][PF$_6$]
Material and Methods

- Experiments in batch flasks
- Analysis of the gas phase
  - A set of closed and sealed bottles was supplied
  - with 1, 2, 3 and 4 µL of VOC (Quijano et al. 2010)

\[
n_{\text{VOC}}^{\text{Total}} = n_{\text{VOC}}^{\text{Liquid}} + n_{\text{VOC}}^{\text{Gas}} \quad \text{Because the system closed}
\]

\[
C_G = KC_L
\]

K measured for DMDS, DMS and toluene in water and IL

\[T = 25^\circ\text{C}, \ 300 \text{ rpm, } 48\text{h}\]
## Results – VOC affinity

### Affinity for VOCs

<table>
<thead>
<tr>
<th>VOC</th>
<th>Liquid phase</th>
<th>K = Cᵣ Cₑ⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMDS</td>
<td>Water</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>[BMIM][PF₆]</td>
<td>0.0013</td>
</tr>
<tr>
<td></td>
<td>[BMIM][NTF₂]</td>
<td>0.0012</td>
</tr>
<tr>
<td>DMS</td>
<td>Water</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>[BMIM][PF₆]</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>[BMIM][NTF₂]</td>
<td>0.009</td>
</tr>
<tr>
<td>Toluene</td>
<td>Water</td>
<td>0.273</td>
</tr>
<tr>
<td></td>
<td>[BMIM][PF₆]</td>
<td>0.00096</td>
</tr>
<tr>
<td></td>
<td>[BMIM][NTF₂]</td>
<td>0.00061</td>
</tr>
</tbody>
</table>

**High affinity**

Similar or even better VOC affinity compared to typical non-aqueous phases like silicone oil, n-hexadecane, di-ethyl-hexyladipate or FC40 (perfluorocarbon).

**DMS lower affinity towards IL**

not selected
Objectives - VOC biodegradation

- **VOC Biodegradation**
  - **Toluene**
  - **DMDS**

  - **Activated sludge** $\Rightarrow$ Emulsion solvent/ water

- Heterotrophic path
- Autotrophic and heterotrophic paths
Material and Methods

VOC biodegradation

120mL glass bottles experiments
2 mL activated sludge
18mL mineral salt medium
5 % IL
and 1 µL of liquid VOC

Gas phase analysis by GC-FID

Sealed (aluminium caps)
Gas phase
Liquid phase (IL)

T = 25°C, 300 rpm 72 h
Results - Biodegradation

Non-acclimated cells

DMDS

- Control – No IL
- [Bmim][PF6]
- [Bmim][NTF2]

Toluene

- Control – No IL
- [Bmim][PF6]
- [Bmim][NTF2]

Cell acclimation is needed
Results - Biodegradation

Acclimated cells

60% depletion of VOC in the gas phase
New injection of 1 µL of liquid VOC
This procedure was repeated during 10 days

- No significant improvement for DMDS
- Improvement of Toluene biodegradation for the control and in [Bmim][PF6]

DMDS

Control – No IL
[Bmim][PF6]
[Bmim][NTF2]

Toluene

Control – No IL
[Bmim][PF6]
[Bmim][NTF2]

Same initial amount of VOC in the controls and in the tests including 5% (v/v) of IL
Nearly similar biodegradation rates:
0.37 g m⁻³ reactor h⁻¹ for control
0.36 g m⁻³ reactor h⁻¹ for 5% IL

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Conclusions

[Bmim][PF₆] and [Bmim][NTF₂] appeared:

- Not biodegradable.

- Not toxic after 24 h acclimation (glucose uptake inhibition): microorganisms recover approximately 100 and 70 % of their metabolic activity (relative to controls) at IL concentrations of 5 and 10 %, respectively.

- High affinity for DMS, DMDS and toluene: partition coefficients comparable or higher than typical liquid solvents used in multiphase bioreactors.
Conclusions

[Bmim][PF₆] and [Bmim][NTF₂]:

- Inhibited the bacterial communities able to metabolize DMDS and toluene, especially towards DMDS-degrading microorganisms.

- Otherwise, sludge acclimation increased VOC biodegradation, particularly for toluene — Similar biodegradation rates for control and in 5% [Bmim][PF6].

Future work:
- More complex acclimation strategies including microbial acclimation to both IL and VOC.
Thank you for your attention

Rennes