Solvent flux behaviour and rejection characteristics of hydrophilic and hydrophobic TiO$_2$ and ZrO$_2$ membranes

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Outline

• Introduction:
  - SRNF – alternative??????
  - Membranes – which are suitable for a detailed transport description????

• Materials and methods:
  - Set – up, solvents, membranes, procedure

• Results and discussion — solvent flux and rejection characteristics through ceramic membranes

• Conclusions: transport mechanism (viscous flow??) and rejection...
Introduction

• **Solvent Resistant Nanofiltration (SRNF)**
  = viable alternative for energy consuming conventional processes (distillation, evaporation...)

• **New SRNF membranes:**
  - Polymeric: swell and crack in non-polar organic solvents
  - Ceramic: better chemical, thermal and mechanical resistance!!!
Materials and methods

• Experimental set – up: cross – flow filtration unit

• Membranes:
  - Hydrophilic TiO\textsubscript{2} (MWCO: 275, 650, 1400 and 7000 Da) manufactured by VITO (Mol, Belgium) and HITK (Hermsdorf, Germany)
  - Hydrophobic ZrO\textsubscript{2} (MWCO: 600 Da) manufactured by HITK (Hermsdorf, Germany)

• Solvents: water, methanol, ethanol, 2-propanol, toluene, n-hexane – selected by molecular size, viscosity and polarity
Materials and methods

- **Solvent flux measurements**
  - **Pressure:**
    - 5 bar for 275, 1400 Da TiO$_2$ and 600 Da ZrO$_2$ membranes
    - 3 bar in case of 7000 Da TiO$_2$ membrane
  - **Temperature range:** 15 – 50° C

- **Rejection measurements**
  - polyethyleneglycols (PEGs) + water
  - brilliant blue (MW=826 Da) + solvent (ethanol)
  - bromothymol blue (MW=624 Da) + solvents (ethanol, toluene)
Materials and methods

Brilliant blue (MW = 826 Da) polar

Bromothymol blue (MW = 624 Da) non-polar
Results: **Hydrophilic TiO$_2$ membranes**

**MWCO: 275 Da**

- Water
- Methanol
- Ethanol
- 2-Propanol
- n-Hexane
- Toluene

**MWCO: 1400 Da**

- Water
- Methanol
- Ethanol
- 2-Propanol
- n-Hexane
- Toluene

**No pure viscous flow**
Results: Hydrophilic TiO$_2$ membranes

MWCO: 275 Da
- Water
- Methanol
- Ethanol
- 2-Propanol
- n-Hexane
- Toluene

MWCO: 1400 Da
- Water
- Methanol
- Ethanol
- 2-Propanol
- n-Hexane
- Toluene

MWCO: 7000 Da
- Toluene
- Methanol
- 2-Propanol
- n-Hexane
- Ethanol
- Water

Viscous flow
Results: Hydrophilic TiO$_2$ membranes

Detailed temperature influence on solvent flux

MWCO: 275 Da

Increase of the flux values with about 100% from 20 to 50°C
### Results: Observed activation energy

<table>
<thead>
<tr>
<th>MWCO [Da]</th>
<th>Solvent</th>
<th>$E_j$ [kJ/mol]</th>
<th>$E_\eta$ [kJ/mol]</th>
<th>$\Delta E$ [kJ/mol]</th>
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<tbody>
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<td>275</td>
<td>Water</td>
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<td>2-propanol</td>
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<td>2-propanol</td>
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<td>Toluene</td>
<td>11.1</td>
<td>9.0</td>
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<td>n-hexane</td>
<td>10.7</td>
<td>6.5</td>
<td>4.3</td>
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</table>
Results: Hydrophobic ZrO$_2$ membrane

MWCO: 600 Da

<table>
<thead>
<tr>
<th>MWCO [Da]</th>
<th>Solvent</th>
<th>$E_J$ [kJ/mol]</th>
<th>$E_\eta$ [kJ/mol]</th>
<th>$\Delta E$ [kJ/mol]</th>
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Viscous flow
### Results: Rejection characteristics

<table>
<thead>
<tr>
<th>Membrane</th>
<th>MWCO</th>
<th>Solute</th>
<th>Solvent</th>
<th>Rejection [%]</th>
<th>Flux [l h⁻¹ m⁻²]</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>25°C</td>
<td>50°C</td>
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<tr>
<td>TiO₂</td>
<td>275</td>
<td>Brilliant blue</td>
<td>Ethanol</td>
<td>99.1</td>
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<td>Ethanol</td>
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<td>62.0</td>
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<td></td>
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<td>Toluene</td>
<td>99.3</td>
<td>99.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>650</td>
<td>Brilliant blue</td>
<td>Ethanol</td>
<td>95.5</td>
<td>98.0</td>
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<td>99.9</td>
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<tr>
<td>ZrO₂</td>
<td>600</td>
<td>Brilliant blue</td>
<td>Ethanol</td>
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<td></td>
<td>Toluene</td>
<td>36.0</td>
<td>40.0</td>
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</tbody>
</table>
Conclusions: Solvent flux

• Hydrophilic TiO$_2$ membranes
  - 275, 1400 Da – permeability and viscosity increased with temperature
  - 7000 Da – the permeation mechanism of solvents obeys the viscous flow
  - Observed activation energies of solvent permeation were larger for membranes with lower MWCO and higher than the activation energies of solvent viscosity

• Hydrophobic ZrO$_2$ membranes
  - Increase of the flux with the temperature attributed to a viscosity decrease
  - Applicable for non-polar organic solvents (high n-hexane and toluene fluxes)
Conclusions: Rejection characteristics

• Temperature does not affect the rejections
• High values for hydrophilic membranes and low for hydrophobic membranes
• Polar brilliant blue rejections in ethanol were the highest (high molecular size of solute, affinity to the membrane surface...)
• Rejection of bromothymol blue (non-polar) was lower in ethanol (more polar) than in the toluene (less polar)!!
Acknowledgements

• K.U.Leuven Research Council (OT/06/37)

• VITO (PhD grant for B.Verrecht)

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