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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

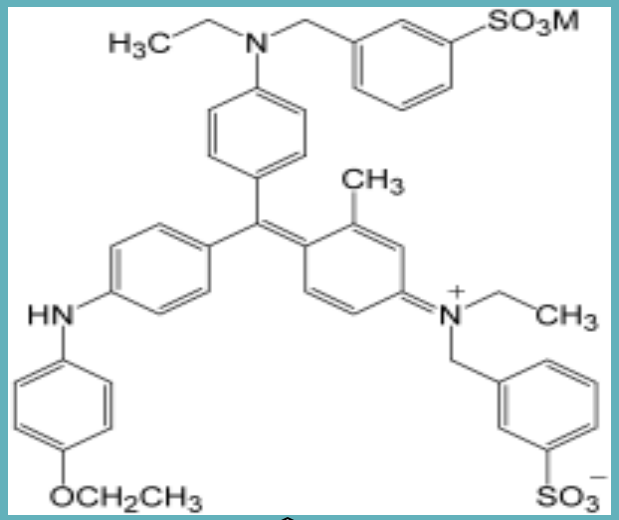
- Experimental set – up: **cross – flow** filtration unit
- Membranes:
  - Hydrophilic TiO_2 (MWCO: 275, 650, 1400 and 7000 Da) manufactured by **VITO** (Mol, Belgium) and **HITK** (Hermsdorf, Germany)
  - Hydrophobic ZrO_2 (MWCO: 600 Da) manufactured by **HITK** (Hermsdorf, Germany)
- Solvents: water, methanol, ethanol, 2-propanol, toluene, n-hexane – selected by molecular size, viscosity and polarity

Materials and methods

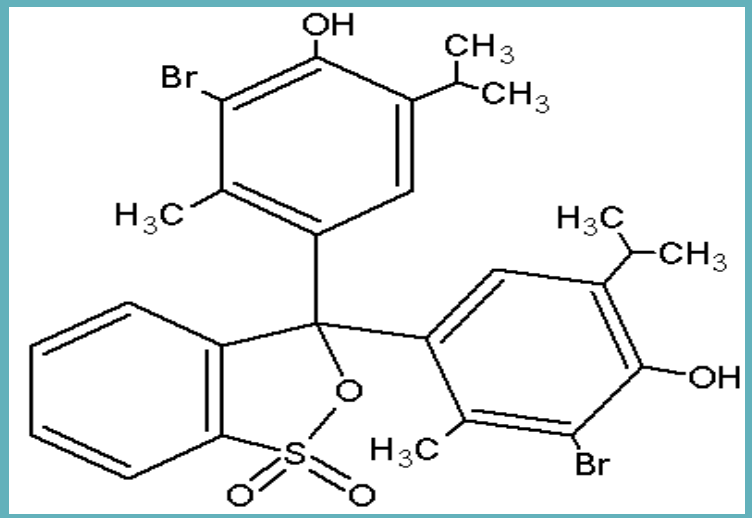
- Solvent flux measurements
  - Pressure:
    5 bar for 275, 1400 Da TiO_2 and 600 Da ZrO_2 membranes

    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

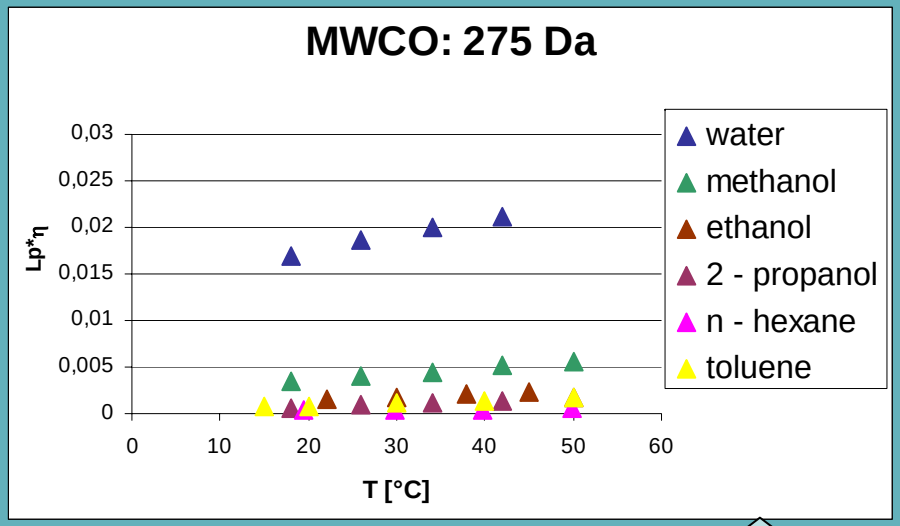


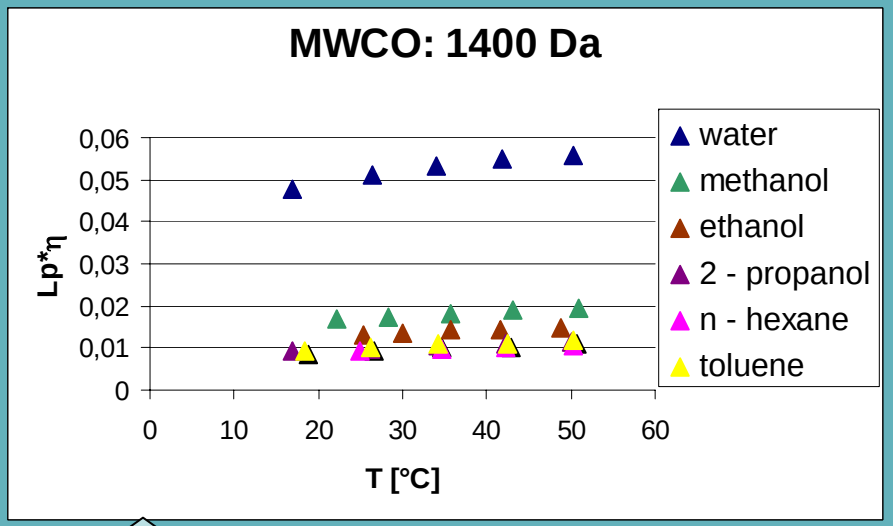
Brilliant blue
(MW = 826 Da)
polar



Bromothymol blue
(MW = 624 Da)
non-polar

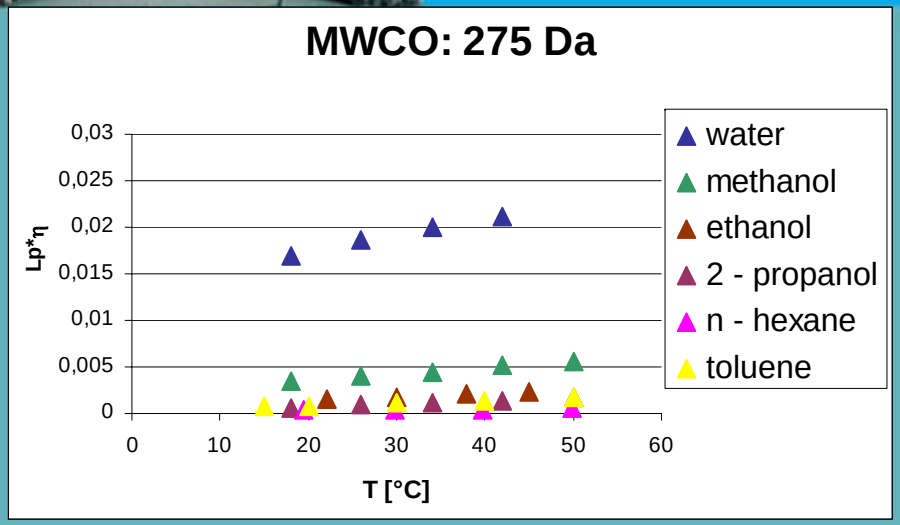
Results: Hydrophilic TiO_2 membranes

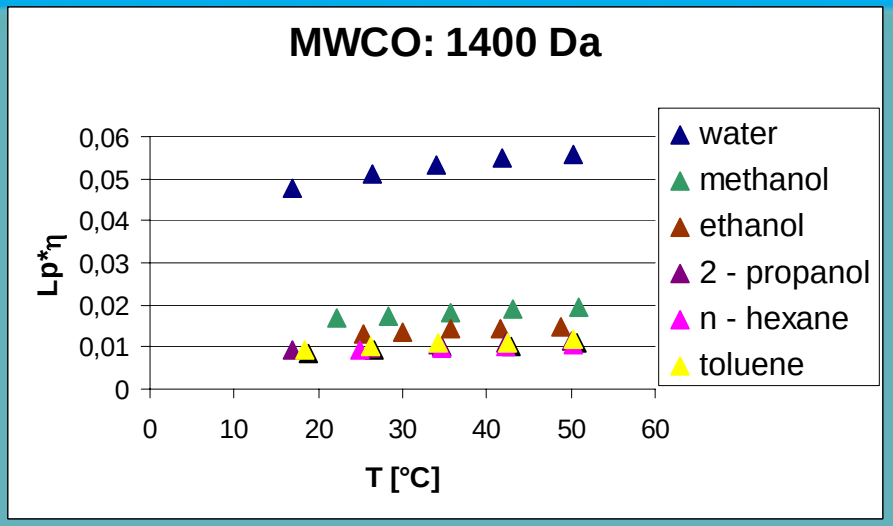


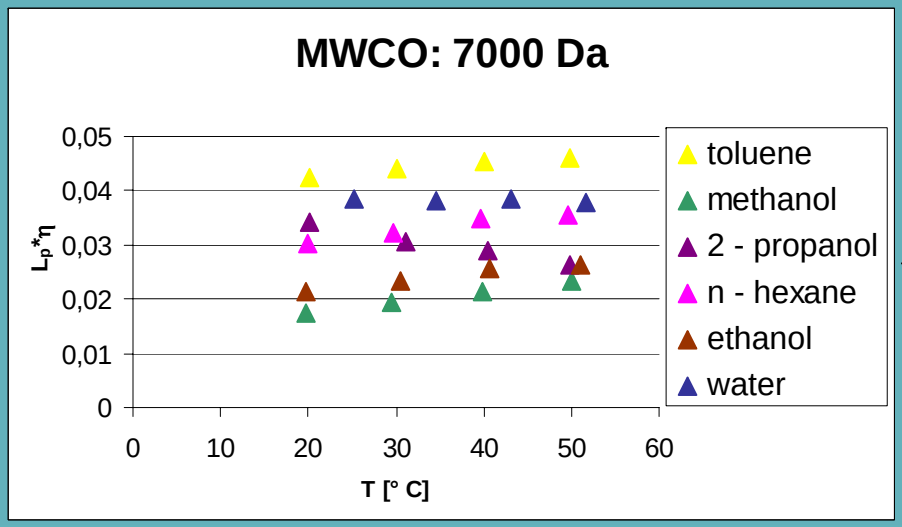


No pure viscous flow

Results: Hydrophilic TiO_2 membranes



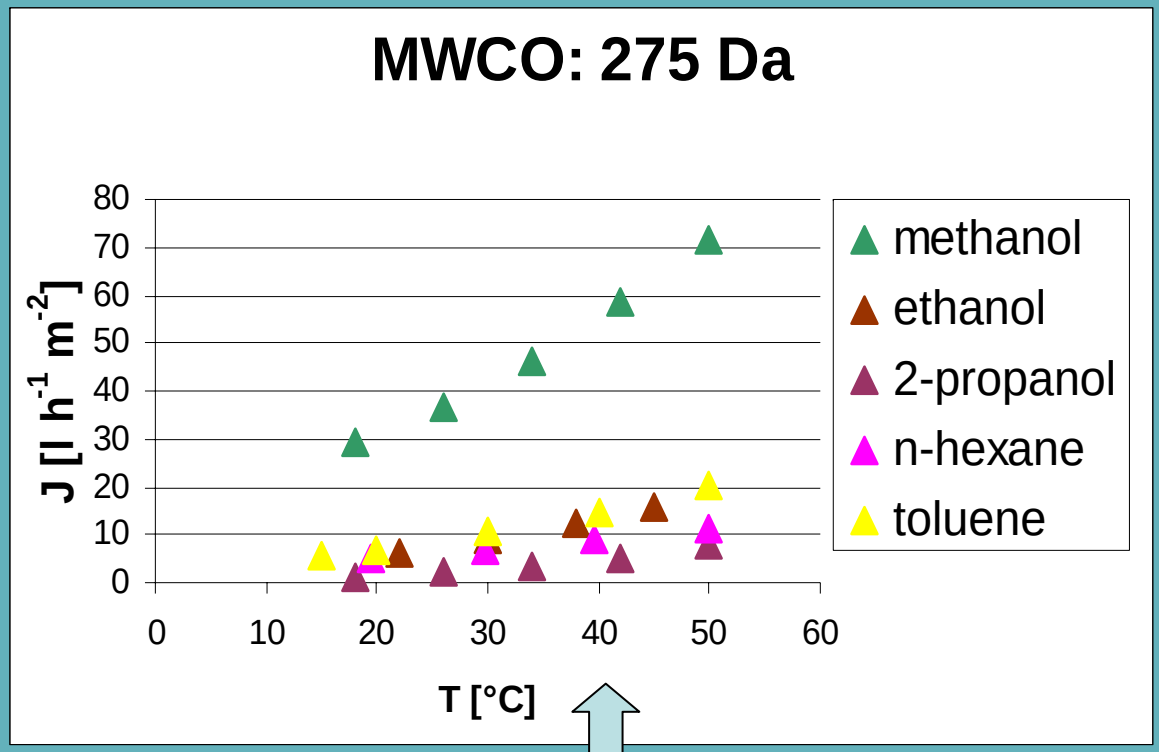




Viscous flow

Results: Hydrophilic TiO_2 membranes

Detailed temperature influenece on solvent flux

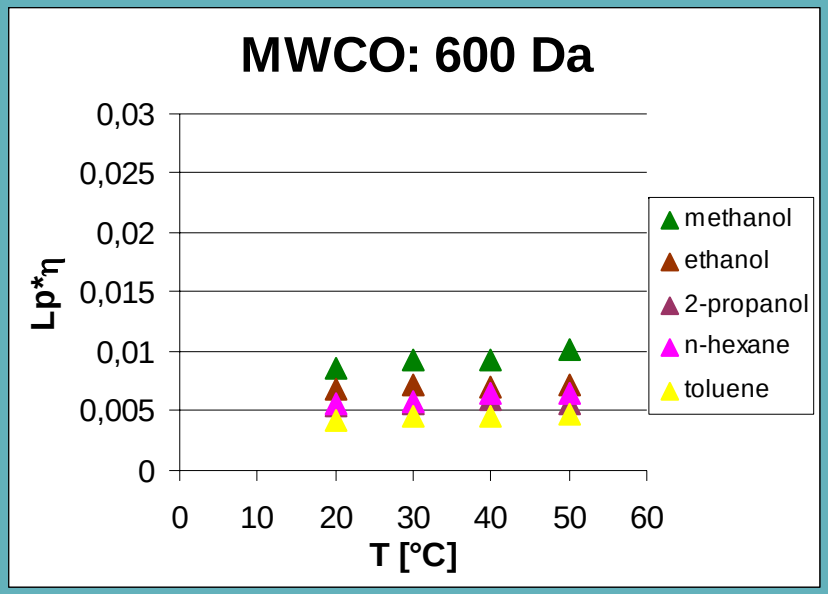


Increase of the flux values with about 100% from 20 to 50° C

Results: Observed activation energy

MWCO [Da]	Solvent	E_J [kJ/mol]	E_η [kJ/mol]	ΔE [kJ/mol]
275	Water	23.0	16.1	6.9
	Methanol	22.1	10.5	11.6
	Ethanol	30.8	14.2	16.6
	2-propanol	43.5	21.5	22.0
	Toluene	28.8	9.0	19.8
	n-hexane	19.4	6.5	12.9
1400	Water	19.7	16.1	3.6
	Methanol	14.3	10.5	3.8
	Ethanol	18.0	14.2	3.8
	2-propanol	26.5	21.5	5.0
	Toluene	14.1	9.0	5.1
	n-hexane	10.3	6.5	3.8
7000	Water	15.3	16.1	-0.8
	Methanol	18.2	10.5	7.6
	Ethanol	19.8	14.2	5.6
	2-propanol	14.8	21.5	-6.6
	Toluene	11.1	9.0	2.1
	n-hexane	10.7	6.5	4.3

Results: Hydrophobic ZrO_2 membrane



Viscous flow

MWCO [Da]	Solvent	E_J [kJ/mol]	E_η [kJ/mol]	ΔE [kJ/mol]
600	Methanol	12.5	10.5	2.0
	Ethanol	14.3	14.2	0.1
	2 – propanol	24.3	21.5	2.8
	Toluene	13.2	9.0	4.2
	n – hexane	8.4	6.5	1.9

Results: Rejection characteristics

Membrane	MWCO	Solute	Solvent	Rejection [%]		Flux [l h^{-1} m^{-2}]	
				25° C	50° C	25° C	50° C
TiO_2	275	Brilliant blue	Ethanol	99.1	98.4	0.8	2.5
		Bromothymol blue	Ethanol	67.0	62.0	1.2	3.2
			Toluene	99.3	99.3	0.2	0.7
TiO_2	650	Brilliant blue	Ethanol	95.5	98.0	0.8	2.4
		Bromothymol blue	Ethanol	55.5	57.0	0.9	2.5
			Toluene	\	99.9	\	0.4
ZrO_2	600	Brilliant blue	Ethanol	70.0	70.0	8.6	1.6
		Bromothymol blue	Ethanol	16.5	18.5	13.7	18.4
			Toluene	36.0	40.0	14.9	21.8

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)

For financial support!!!!