Hybrid silica nanofiltration membranes with low MCWO values

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1 Introduction

In industrial processes there is a need for solvent stable nanofiltration membranes with a molecular weight cut-off value of only a few hundred Daltons. By using these membranes important process improvements and energy savings are possible as compared to e.g. thermal separation processes. Developments nowadays are focussing towards (1) stabilising polymeric membranes, (2) using ceramic and modified ceramic materials, and towards (3) applying hybrid membranes. Because of their unique solvent resistance, we have selected hybrid silica membrane materials as a basis for developing solvent stable nanofiltration membranes that meet the demands as set by industry.

Here we will report on successfully tuning the pore size of the final membrane layer by using a hybrid silica precursor (BTESE, bis-tri-ethoxy-silyl-ethane) and by using additives/templates. Characterisation results will be presented including SEM analysis, flux and retention measurements. Relations between different preparation parameters and the membrane performance will be presented. Most importantly, it will be shown that it is possible to prepare hybrid silica nanofiltration membranes with a high retention for molecules with a molecular weight of < 400 Dalton.

2 Experimental

Membrane preparation

The membranes have been prepared via sol-gel technology and coating on the outside of a porous single hole α-Al_2O_3 tube onto which first two macro-porous α-Al_2O_3 layers and one meso-porous γ-Al_2O_3 layer were coated as described by Bonekamp [1]. This product with a length of 30 cm was subsequently used as a support for the hybrid silica (HybSi®) membrane. The final membrane layer was made based upon BTESE (bis-tri-ethoxy-silyl-ethane) as precursor. This membrane was previously developed for pervaporation applications (dehydration of organic solvents and acids) and has proven to combine a high performance with superior stability [2, 3]. For nanofiltration applications the pores of this membrane are too small and the idea is to incorporate a micelle/ionic surfactant like molecule (CTAB – Cetyl-trimethyl-ammonium-bromide) into the sol to create a more open and meso-porous pore structure [4]. The prepared sol was applied on the outside of the support system via dip coating technology and after drying it was subsequently heat treated to consolidate the porous system.

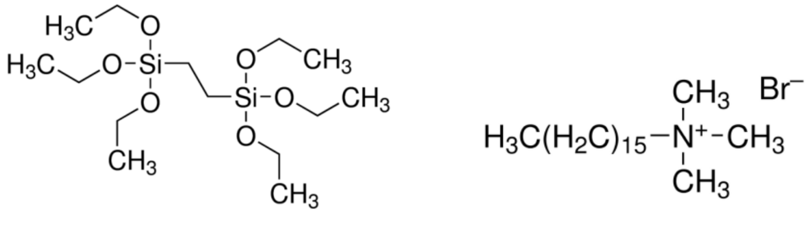

Figure 1: Precursor BTESE and CTAB as pore former

Retention measurements

In the retention tests a liquid (water) feed was used, the feed was pressurized up to maximum 30 bars and the flow (l/h) through the membrane (30 cm length) was measured for either a pure solvent or the solution containing 1 wt.% of PEG. The permeance (l/m^{2}hbar) was calculated using the membrane area and the pressure difference over the membrane. The permeate was at atmospheric pressure. The retention values were calculated using the permeate concentration and the concentration of the original feed solution according to the equation:

$$\%Retention = (1 - (\frac{Conc.PEG\ permeate}{Conc.PEG\ feed}))*100\% \quad (1)$$

An HPLC method was used for analysing the PEG solutions consisting of a number of different molecular weight PEGs: 200, 600, 2000 and 10000 Dalton of 1 wt.% of each PEG in water. For solutions in which only one molecular weight of PEG was used a refractive index analyser, Mettler Toledo RA510M, was used. The molecular weight cut-off (MWCO) value for the membranes is defined as the molecular weight at which 90% of the molecules is retained by the membrane.

3 Results and discussion

First trail

A first membrane made based upon a mixture of BTESE and CTAB as precursors had a thickness of about 1.2 µm, which is very thick. The retention was about 180 Dalton (see Figure 2) and the water permeance was only 0.006 l/m^{2}hbar, which is very low. Industrial applications would require a permeance in the order of 0.5 l/m^{2}hbar.

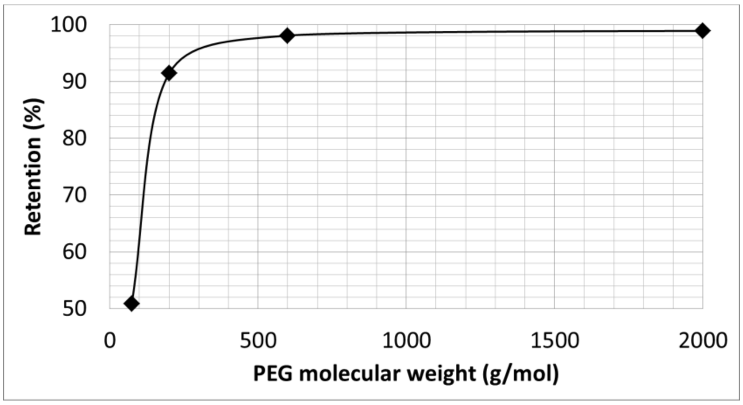

Figure 2: Retention for BTESE+CTAB membrane measured by using different PEG molecules in water.

Optimisation of the performance has been done by making changes in the sol recipe like the relative amounts of BTESE, CTAB, acid and water, by changing the coating conditions, and by optimising the membrane layer thickness. Below some trends will be presented.

Layer thickness optimisation

The membrane layer thickness can be modified by using different sol concentrations. The results as presented in Table 1 indicate that a decrease of the thickness of a factor of 250 only leads to a flux increase by a factor of about 2.5 while the retention, remains low and does not change significantly. Probably (partly) infiltration of the sol into the porous sub-structure leads to a high resistance for transport and thus the influence of the final membrane layer thickness on the flux/permeance is small. SEM pictures of some of the membranes that have been prepared are presented in Figure 3.

Membrane	Thickness (nm)	Water permeance (kg/m^2hbar)	MWCO for PEG in water (Dalton)
1	1220	0.006	190
2	375	0.009	180
3	15	0.01	180
4	< 5	0.015	180

Table 1: influence of membrane thickness on the performance

The acetone permeance for membrane No. 4 was 0.16 l/m^2hbar at room temperature and increases to 0.26 l/m^2hbar at 60°C. This permeance increase with temperature can be explained by the decrease in the viscosity of acetone.

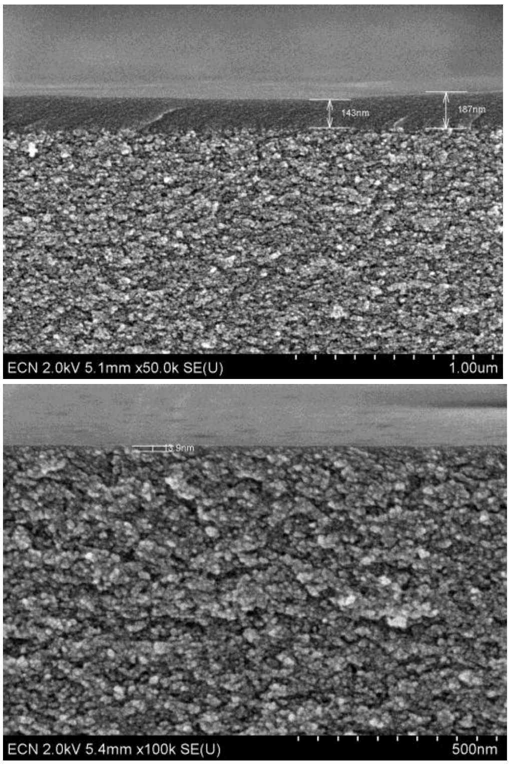

Figure 3: Membranes made at different sol concentrations, left 100% and right 50%.

Sol modification

The concentration of CTAB as component to increase the pore size from micro-porous to meso-porous was found to be critical. At low concentrations a membrane was obtained that is very selective in the dehydration of organic solvents by pervaporation. This membrane is expected to be micro-porous. At higher CTAB concentrations the membrane quality shifts from pervaporation to nanofiltration. Further increase of the micelle concentration leads to unstable sols that flocculate and which are not suitable for membrane preparation. The most optimal CTAB concentration is about 0.2 mol/l which is close to the reported critical micelle concentration for CTAB in ethanol of 0.24 mol/l [5].

Another important parameter is the ratio water : ethoxy in the original precursor. It was found that at lower hydrolysis ratios an improved nanofiltration membrane is obtained as compared to higher hydrolysis ratios. The main reason for this shift seems to be that at lower hydrolysis ratios a less viscous sol is obtained leading to a layer that has a more open structure but is also more infiltrated into the support, see Figure 4. Furthermore these lower hydrolysis ratios lead to nanofiltration membranes with a lower MWCO and increased permeance, see Table 2. The water permeance is still rather low though.

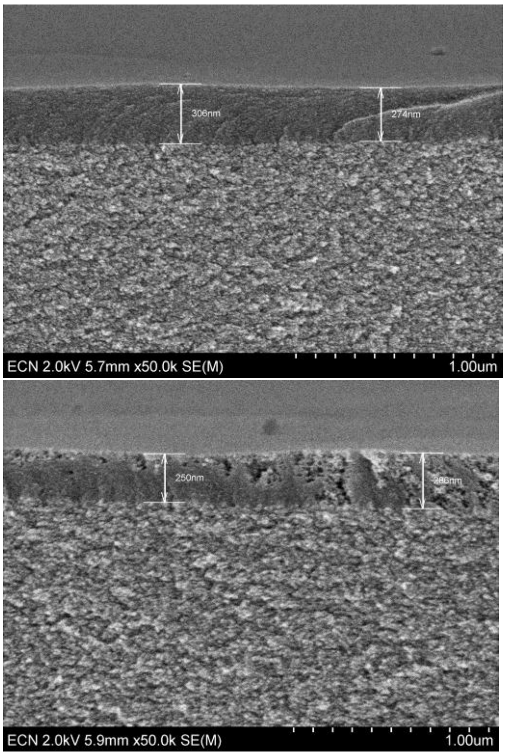

Figure 4: Membranes made at different water : ethoxy ratio’s, left 2.0 and right 0.75.

Hydrolysis ratio	Thickness (nm)	Water permeance (kg/m^2hbar)	Retention for PEG 200 in H_2O (Dalton)	Retention for PEG 1000 in H_2O (Dalton)

2.0	275	0.003-0.008	57%	84%
0.75	~250 infiltrated	0.02-0.06	65%	93%

Table 2: Influence of hydrolysis ratio on the membrane performance

4 Conclusions

Hybrid silica membranes based on BTESE can be tailored towards nanofiltration membranes by using pore formers like CTAB. A retention of only a few 100 Dalton is possible. The water permeance has to be increased by a factor of 10 for industrial applications. The low permeance is probably caused by infiltration of the sol that is used to prepare the final membrane layer into the support, as the thickness of the membrane layer only has a small influence on the permeance. The acetone permeance is promising.

References

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