



From hydrophilic to hydrophobic HybSi[®] membranes: A change of affinity and applicability

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ABSTRACT

The present study describes the effect of the presence of terminating alkyl groups on the performance of organic–inorganic hybrid silica membranes. By incorporation of different R-triethoxysilanes ($R=C_1$ to C_{10} alkyl) into 1,2-bis(triethoxysilyl)ethane (BTESE) based materials the affinity could be tailored from hydrophilic to hydrophobic. The separation properties of the membrane based on these materials was found to be strongly dependent on the length of the R-group. Gas permeance measurements indicated reduced molecular sieving properties and an enhanced affinity for CO_2 for longer R-groups. Longer R-groups also resulted in lower permeate water purity, falling from >99 wt% for BTESE to ~ 40 wt% for C_{10} in the dehydration of *n*-butanol/water (95/5 wt%) by pervaporation. Concomitantly, the permeate *n*-butanol purity in the pervaporation of *n*-butanol/water mixtures (6.8 wt% of *n*-butanol) increased to a value of >40 wt% for $R=C_{10}$. This membrane exhibited constant separation factors over a large range of temperatures (30 to 90 °C) and *n*-butanol feed concentrations (0.5 to 6.8 wt%). By increasing the temperature from 30 to 90 °C, the *n*-butanol flux reached a value as high as 3 kg/m² h for a feed mixture containing 4.5 wt% of *n*-butanol.

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1. Introduction

The separation or purification of alcohol/water mixtures is performed using capital- and energy-intensive distillation. To replace distillation, less energy demanding separation processes as gas stripping, steam stripping, liquid–liquid extraction can be used [1,2]. Among them, also organophilic pervaporation is considered to be a viable alternative for alcohols separation from aqueous solutions [1–3]. The membrane development has been focused on hydrophobic, polymeric materials [1,3–6]. Recently, we developed hybrid organic–inorganic HybSi[®] membranes to overcome the stability boundaries of inorganic silica [7]. The introduction of an organic fragment in a silica network by using ethylene-bridged bis-silane precursors lead to membranes having a life time of over 1000 days in alcohol dehydration at high temperatures (150 °C) without a decrease in the selectivity [8]. The intrinsic hydrophilicity of this bridged organic silica limits the applicability of these membranes to the separation of polar from less polar molecules. However, by changing the nature/structure of the precursors and the content of organic fragments in the

hybrid silica network, the membrane behavior can be controlled [9–11]. For example, the introduction of functional amine groups in the network resulted in highly water-permeable hydrophilic membranes [11]. This implies that the incorporation of well-defined organic groups can be used to tailor the membrane affinity to specific applications. In the current study, we aim to develop intrinsically hydrophobic membranes by the introduction of precursors with large organic fragments in the hybrid silica network. Combined with the proven solvent and water stability of the hybrid membrane material, this approach was designed to result in stable hydrophobic hybrid silica membranes that would be suitable for a range of solvent separation processes. Such processes include upgrading of bioalcohol/water mixtures to fuel grade and harvesting of valuable alcohols from aqueous process streams [12,13].

Here, we present the development and characterization of such hydrophobic membranes. The membranes were developed starting from the precursor 1,2-bis(triethoxysilyl)ethane (BTESE). This precursor with a bridging organic group is commonly used for the preparation of hydrophilic hybrid silica HybSi[®] membranes. To introduce an hydrophobic character in these membranes, terminating alkyl-groups, R-triethoxysilanes (RTES, $R=C_1$ to C_{10} alkyl), were added during the preparation (Fig. 1). The relations between the alkyl chain length, the pore size and the

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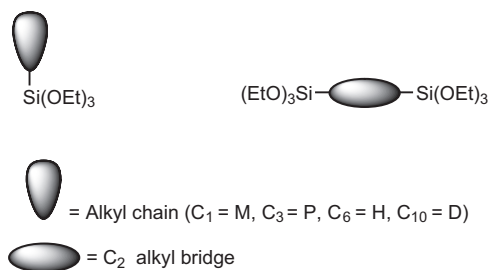


Fig. 1. Precursors used in this study.

affinity of the membranes were studied. The performances of all membranes in pervaporation were measured in the dehydration of *n*-butanol for butanol-rich mixtures, and in the recovery of *n*-butanol for water-rich mixtures. The influence of the operating conditions on the performance of the most promising membrane was subsequently determined. Finally, the applicability of these membranes in bio-butanol recovery from fermentation broths is compared to other organophilic membranes.

2. Experimental

2.1. Materials

1,2-Bis(triethoxysilyl)ethane (E, ABCR, 97 wt%), methyltriethoxysilane (M, ABCR, 98 wt%), *n*-propyltriethoxysilane (P, ABCR, 97 wt%), *n*-hexyltriethoxysilane (H, ABCR, 95 wt%), *n*-decyltriethoxysilane (D, ABCR, 97%), nitric acid (69 wt%, Aldrich), and EtOH (p.a., Aldrich) were used as received. Water was deionized at 18 MΩ/cm using a Millipore purification system. Pervaporation measurements were performed with distilled water and *n*-butanol (P.A. grade) from Aldrich. The membranes are further named according to the precursors used: the letter E refers to pure BTESE membranes and for the other membranes the letters M, P, H, D refer to the alkyltriethoxysilanes introduced in the BTESE-based hybrid silica network. The precursors were present in equimolar ratios.

2.2. Membrane development

The BTESE/RTES mixed sols were synthesized according to a two-step synthesis procedure. In all cases, the preparations were started by mixing the required amounts of nitric acid and water, and by diluting, the 1:1 ratio of BTESE and RTES precursors with ethanol. Half of the acid/water mixture was then added dropwise under stirring to the precursor/EtOH mixture, and kept at 333 K under continuous stirring for 1.5 h. Subsequently, the second half of the acid/water mixture was added dropwise, while keeping the mixture at 333 K, after which this mixture was stirred during another 1.5 h at 333 K. All the sols were synthesized with overall compositional ratios of $\text{Si}/\text{EtOH}/\text{H}^+/\text{H}_2\text{O} = 1/6.36/0.08/3$.

After adjustment of the silica sol concentration, sols were filtered over 0.8 μm cellulose acetate filters (Whatman®). Membrane coatings were applied in a class-1000 cleanroom on the outside of 30 cm long tubular supports composed of α-Al₂O₃ layers and a final smooth mesoporous γ-Al₂O₃ layer [14]. After overnight drying in the clean room, the membranes were heat treated at 523 K under N₂ for two hours with heating and cooling rates of 0.5 °C/min. Four cycles of vacuum/N₂ purge of one hour each were performed before the start of the heat treatment. All membranes were sealed using stainless steel caps and graphite as packing material [15].

2.3. Supported film characterization

Layer thickness determinations and surface observations were carried out on samples taken from the middle of the heat treated membranes by means of a high resolution JEOL JSM-6330F Field Emission scanning Electron Microscope (SEM). Single gas permeance measurements were performed at 523, 423 and 323 K with feed pressures from 3 to 9 bara. Pressure differences of 2 bara were applied except for the point at 3 bara feed pressure for which a pressure difference of 1.5 bar was used. A bleed of 50 ml/min was applied for all measurements. Measurements were performed using H₂, N₂, and CO₂ (99.999 mol% pure). Before starting the measurement, each membrane was dried in the setup for two hours at 523 K under N₂. H₂ permeance measurements were performed both as first and last measurement. The gas permeabilities were calculated based on the permeances and the layer thicknesses measured by SEM. The pictures of deionized water drops were taken at a fixed distance with drops of 10 μl deposited manually on the surface of the tubular membranes using a Mettler Toledo micro-pipette.

2.4. Membrane performance

The pervaporation measurements were performed on a standard glass pervaporation setup, as described in detail by Van Veen [8]. The *n*-butanol dehydration measurements were carried out with an *n*-butanol/water (95/5 wt%) feed mixture at 368 K. The *n*-butanol enrichment pervaporation measurements were performed with *n*-butanol/water feed mixtures ranging from 0.5/99.5 wt% to 7/93 wt%. Measurement temperatures for these measurements were 303, 333 and, 363 K. In all cases, the permeate pressure was kept constant at 10 mbar and measurements were performed after stabilization. Feed and permeate compositions were determined using refractive index measurements on a Mettler Toledo RA510M device. The *n*-butanol/water permeate samples that exhibited two phases were homogenized by addition of a known amount of water before the refractive index determination. Overall pervaporation process selectivities (α_{process}) were analyzed as a combination of the evaporation separation factor (α_{evap}) and the intrinsic membrane separation factor (α_{mem}) [16,17]:

$$\alpha_{\text{process}} = \alpha_{\text{evap}} \times \alpha_{\text{mem}} \quad (1)$$

with:

$$\alpha_{\text{evap}} = \frac{P_b/P_w}{n_b/n_w} \quad (2)$$

and

$$\alpha_{\text{mem}} = \frac{P_{\text{bp}}/P_{\text{wp}}}{P_b/P_w} \quad (3)$$

with P_b and P_w the partial pressure in the vapor phase on the feed side of *n*-butanol (b) and water (w); n_b and n_w the molar fraction of *n*-butanol (b) and water (w) at the feed side liquid phase, and P_{bp} and P_{wp} the partial pressures of *n*-butanol (b) and water (w) in the permeate. The vapor liquid equilibrium (VLE) calculations necessary to determine the evaporation separation factor were performed with Aspen Plus v7.2. The vapor pressure was calculated with the extended Antoine vapor pressure equation, with the UNIQUAC thermodynamic model of Aspen Plus. The interaction parameters that have been used for water (1)/ *n*-butanol (2) binary mixture are as follow:

$$A_{1,2} = 0; A_{2,1} = 0; B_{1,2} = -276.1; B_{2,1} = 9.1794;$$

These parameters are taken from Aspen Plus data bank LLE-LIT. According to data bank the parameters were fitted based on

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