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Pushing membrane stability boundaries with HybSi[®] pervaporation membranes

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journal homepage: www.elsevier.com/locate/memsciPushing membrane stability boundaries with HybSi[®] pervaporation membranesHenk M. van Veen^a, Marielle D.A. Rietkerk^a, Donough P. Shanahan^a, Marc M.A. van Tuel^a, Robert Kreiter^a, Hessel L. Castricum^{b,c}, Johan E. ten Elshof^b, Jaap F. Vente^{a,*}^a Energy Research Centre of the Netherlands, Unit: Efficiency and Infrastructure, Membrane Technology Group, P.O. Box 1, 1755 ZG Petten, The Netherlands^b University of Twente, Inorganic Materials Science, MESA+ Institute for Nanotechnology, Department of Science and Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands^c University of Amsterdam, Van't Hoff Institute for Molecular Sciences, Faculty of Science, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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ABSTRACT

To overcome the limitations of currently available commercial polymer and zeolite membranes for pervaporation applications, a hybrid silica membrane (HybSi[®]) has been developed. In this paper the unprecedented stability of HybSi[®] membrane technology for the dehydration of organic solvents is reported. It is shown that the HybSi[®] membranes are suitable for demanding separations using pervaporation at temperatures up to at least 190 °C, in aggressive aprotic solvents including *N*-methyl-2-pyrrolidone (NMP), and down to a pH value of ~2. The high hydrothermal and chemical stability was proven in continuous measurements that lasted for periods of months to several years. The longest test, on the dehydration of *n*-butanol at 150 °C, lasted for 1000 days. The high stability parallels high fluxes and selectivities that meet current industrial demands and expectations. After a period of stabilization, fluxes and selectivities become constant. The presented results show that HybSi[®] membranes are widely applicable in the dehydration of organic solvents by pervaporation.

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1. Introduction

Reduction of CO₂ emissions is a key objective for main governments worldwide. The International Energy Agency (IEA) aims at a reduction by ~50 Gt/year by 2050 [1] for future energy technologies. The 27 EU states decided on a 20% overall boost in renewable fuel use by 2020. In another key measure EU leaders decided to cut carbon dioxide emissions of 1990 by 20% in 2020 [2]. The (petro)chemical sectors are by far the largest energy consumer in the industrial sector, with a share of more than 30% of the total industrial energy consumption. These sectors are facing the challenges of decreasing energy use and reducing CO₂ emissions for economic and environmental reasons [3]. As molecular separation technologies require large amounts of energy, break-through separation technologies are required to reduce the carbon footprint. Membrane technology is generally accepted to play a crucial role in the transition to a sustainable chemical industry [4].

Dehydration of organics in azeotropic mixtures containing water is a potential candidate for energy efficiency improvement using membranes. Pervaporation (PV), vapor permeation (VP), or distillation in combination with one of these membrane processes are suitable energy efficient options for such applications [5,6].

The origin of the higher energy efficiency compared to distillation can be found in the fact that only a part of the feed is evaporated and that no reflux is needed. Furthermore, membrane operation is not hindered by the presence of an azeotrope. Commercial pervaporation and vapor permeation installations [7] utilize polymeric membranes, like polyvinylalcohol (Sulzer Chemtech) [8–10,12,13], polyimide (Vaperma) [13], perfluoropolymers (MTR and Compact Membrane Systems) and polyelectrolytes (GKSS) [10,13] or ceramic membranes, like zeolite A (Mitsui, Mitsubishi, Inocermic) [9,11–13] and silica (Pervatech, Sulzer Chemtech) [10,11,13]. All types of membranes have been used in a wide variety of pervaporation applications. Current successful applications include the dehydration of for example alcohols or ketones, mainly as an end-of-pipe application [7]. Important limitations of these membranes as currently perceived by end-users, are a too low stability at high temperatures, in aggressive solvents, acids, and condensation of the vapor feed. As a result, VP and PV membranes are considered as high risk unit operations, especially in new and more process integrated applications and are not widely regarded as a reliable technology. Consequently, their impact on process- and energy-efficiency improvement, CO₂ emission and cost reduction, has not reached its full potential.

In order to accomplish general acceptance of PV and VP technologies, membrane developers face a number of challenges regarding the applicability at higher temperatures, in a wider pH window, in more aggressive aprotic solvents, and in a wider range

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of water concentrations. Furthermore, membrane sensitivity to a condensing feed during start up and cool down procedures needs to be addressed. As these conditions can appear simultaneously in a separation process it is preferred that one single membrane type can meet all of these criteria. We recently explored the use of organic–inorganic hybrid silica as microporous dehydration membranes. The strategy for this membrane development was to replace part of the silicon–oxygen–silicon bonds in inorganic silica, which are vulnerable to hydrolytic attack, by silicon–hydrocarbon–silicon bridges that do not react with water. Unprecedented life times of at least two years in the dewatering of *n*-butanol at 150 °C were obtained for these so-called HybSi® membranes [14]. The applicability of these membranes for the dehydration of ethanol has been proven, as well as short term stability in the presence of acetic acid [15] and in the presence of limited amounts of nitric acid [16].

Here, the results of a study to explore the stability boundaries of the HybSi® pervaporation membranes under various conditions are reported. The focus of the data presented is on the long-term dewatering of organic solvents at higher temperatures in the presence of organic and mineral acids. Furthermore, stability in the dehydration of a strong aprotic solvent *N*-methyl-2-pyrrolidone (NMP) is demonstrated. All tests were performed continuously, i.e., 24 h a day, 7 days a week, for periods up to almost 3 years.

2. Experimental

2.1. Membrane preparation and characterization

The preparation of HybSi® membranes has been described in detail elsewhere [14–19]. On the outside of a porous single hole α -Al₂O₃ tube (Tami) two macroporous α -Al₂O₃ layers and one mesoporous γ -Al₂O₃ layer were coated as described by Bonekamp [20]. This product was subsequently used as a support for the HybSi® membrane.

Throughout this paper, the performances of three types of HybSi® membrane with different chemical compositions are discussed. This composition is determined by the precursors in the sol used for the HybSi® layers. Layers containing either pure bis(triethoxysilyl)methane (BTESM), pure bis(triethoxysilyl)ethane (BTESE), or a 50/50 mol.% mixture of BTESE and methyltriethoxysilane (MTES) were made (Fig. 1). The long term performance of these membranes was studied in various solvent/water mixtures at several temperatures and with varying acid concentrations. During the long term tests no membranes were replaced e.g., because of membrane failure. All membranes that were selected for the tests survived over the complete test period, unless stated specifically in the text.

Pore size distributions of the hybrid silica layers were assessed by permporometry and calculated using the Kelvin equation [15]. In these measurements helium was used as permeating gas and water as condensable gas. High resolution Scanning Electron Microscopy was carried out on a Jeol 6330F SEM equipped with a Noran Voyager EDX at a voltage of 5.0 kV.

2.2. Pervaporation testing

For pervaporation testing a batch test installation developed in house was used, in which a membrane is contained in a vessel with the test liquid (Fig. 2). The feed vessel (1), made of glass for atmospheric conditions, and of stainless steel for pressurized testing was placed on a heater/stirrer (2). A stirring speed of 1100 rpm was used to ensure turbulence on the feed side of the membrane. The temperature was monitored and controlled by a thermocouple (3). The membranes (4), with an area ~ 50 cm², were sealed by using either Kel-F cups and NBR or Kalrez® rubber O-rings for lower temperatures, or a stainless steel cup and graphite compression seal for high temperature operation. The sealing is applied directly on the membrane layer. The test system consists further of 2 sampling vessels (5 and 6) and a larger vessel (7) for continuous measurements. Cold traps (liquid nitrogen) were used to collect the permeate in the sample vessels. The permeate pressure, which is controlled by a vacuum pump (8) and a valve (10), can be measured with a pressure gauge (9). The permeate pressure was kept constant at ~ 10 mbar.

During the prolonged batch pervaporation experiments water was added continuously with a pump in order to keep the feed water content and driving force within one long term experiment constant. For measurements under acidic conditions, the acids were added manually. The membrane performance was determined at regular intervals. The total flux (kg/m² h) was determined by measuring the weight gained in a sample vessel during a certain period of time (in general 10–30 min). The water concentrations of the feed and the permeate were determined from the refractive index at ambient conditions (Mettler Toledo RA510M) for binary mixtures, or by Karl Fischer titration (Metrohm 720 KFS Titrino) for multi-component mixtures. For reasons of comparison, small variations in the feed water concentration were recalculated to a constant water content in the feed, with a linear relation between flux and concentration. In the experiments in which a feed of water, alcohol and an acid was used, regularly the feed and permeate acid concentrations were checked by using pH-paper. Besides this batch set up a continuous flow set up has been used. This set up has been described elsewhere in detail [25]. In this continuous flow setup a larger feed volume (50 l) was pumped/cycled over 6 individual membrane modules with a flow rate of 1000 l/h. To make up for permeate losses and to keep the driving force constant, water was added to the feed vessel at regular intervals. Thus, both in the batch and continuous set-up the pervaporation process ran 24 h/day, in the batch system the membrane was in a stirred feed vessel, while in the continuous set-up the feed was pumped over the membrane and the retentate was recycled back to the feed vessel.

Throughout this paper, the (long term) testing results are presented in the form of water flux and water concentration in the permeate as a function of time, unless otherwise stated. The fluctuations that appear in the graphs are generally caused by small changes in the temperature, the vacuum pressure, or deviations from the ideal linear relationship described above. Quoted pH values of mixtures were calculated assuming equivalent dissociation behavior of the acid as in pure water. For nitric and methylsulfonic

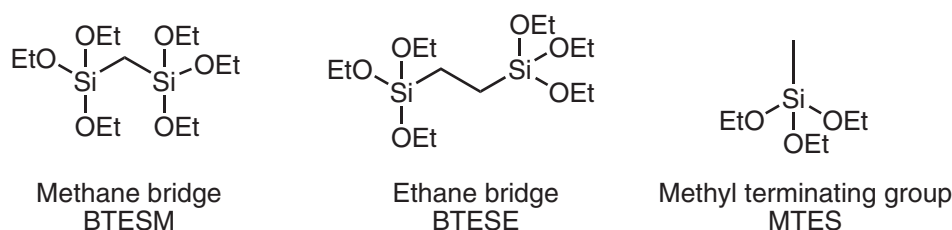


Fig. 1. Precursors used for the HybSi® membrane layer, bis(triethoxysilyl)methane (BTESM), 1,2-bis(triethoxysilyl)ethane (BTESE), and methyltriethoxysilane (MTES).

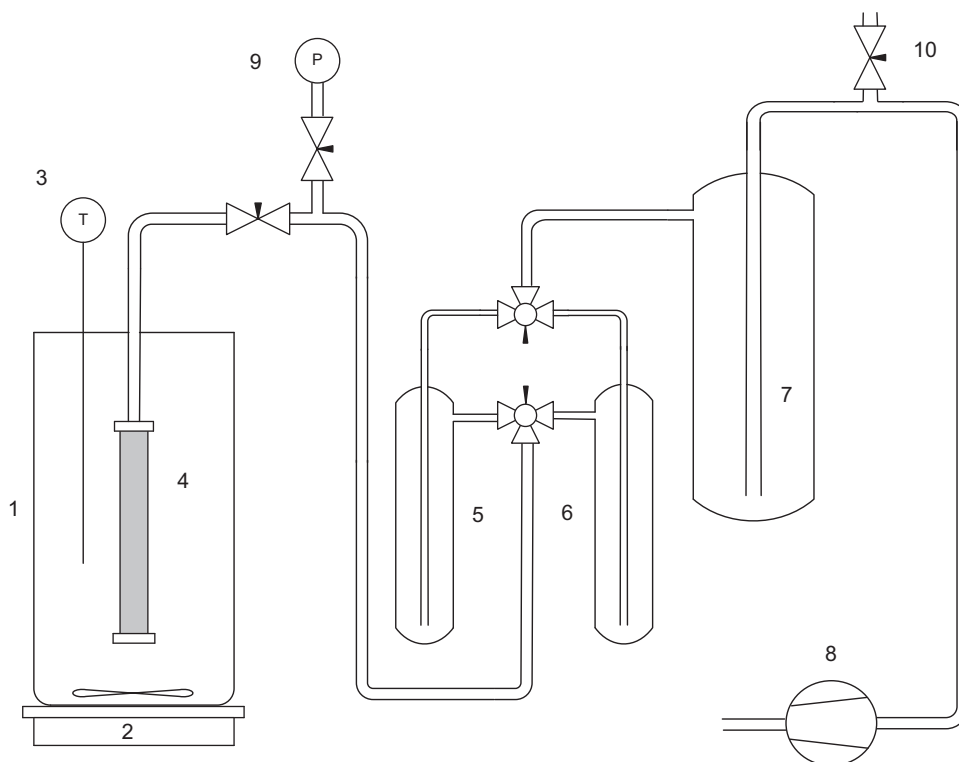


Fig. 2. Schematic drawing of the batch pervaporation test installation.

acid, total dissociation is assumed, whereas for acetic acid partial dissociation is calculated based on the pK_a value of 4.75.

3. Results and discussion

3.1. Membrane preparation

In this study membranes were used that have layer thicknesses in the range of 300–600 nm. Fig. 3 shows, from left to right, the macroporous α - Al_2O_3 support, the γ - Al_2O_3 layer, with a thickness $\sim 2 \mu m$, and finally the functional hybrid silica membrane layer. The average pore size is about 0.5 nm as measured by permoporometry. In general, these membranes have pore size distributions that extend to about 1 nm. The average pore size for membranes made using a BTESE precursor is somewhat smaller than for BTESE membranes. The combined BTESE/MTES precursors lead to the smallest average pore size, but also to a wider pore size distribution. Previous

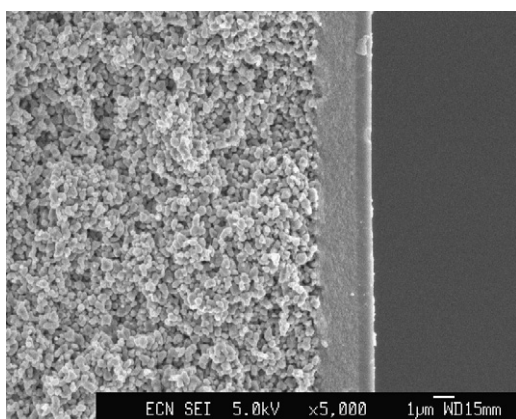


Fig. 3. SEM micrograph (magnification 5000 $\times$) of a hybrid silica layer (BTESE precursor) on the support system.

studies have shown that by changing the sol synthesis conditions, the sol particle size can be modified. Even though there is no direct relation between the particle size and the pore size, the colloid size is important for the fabrication of a functional membrane [15,16,19].

3.2. Long term membrane performance testing

3.2.1. High temperature testing

The high temperature stability of a BTESE/MTES membrane was tested by using a mixture of 3 wt.% water in *n*-butanol at 150 °C in the batch test setup. The membrane was kept on stream continuously for about 950 days. The pervaporation process was then shut down and restarted several times until the membrane had been on stream for ~ 1000 days (Fig. 4a). During the shutdown and restart cycles, the membrane was cooled down to ambient temperature and subsequently reheated to 150 °C. The concentration of water in the permeate increased from initially 90 wt.% water to 96 wt.% within the first 50 days. During the first 200 days of operation, the water flux decreased to $\sim 50\%$ of the initial flux. Similar behavior was reported for methylated silica membranes [21]. After 500 days, the performance of the membrane showed only a gradual change, and after almost 1000 days at 150 °C the membrane was still highly selective and permeable to water. To the best of our knowledge, this is the longest continuous measurement ever reported under these demanding pervaporation conditions. In addition to the long continuous operating period and the higher applied temperature, the HybSi[®] membrane could withstand shutdown and restart procedures without changes in the performance. The results in the batch testing setup were reproduced in the continuous flow testing setup for a similar BTESE/MTES membrane under similar conditions (Fig. 4b). The results again show an increase in the water concentration in the permeate during the first period of testing, accompanied by a gradual decrease of the water flux.

Further testing on another BTESE/MTES membrane was performed, using 3 wt.% water in *n*-butanol at 190 °C (Fig. 5), leading to

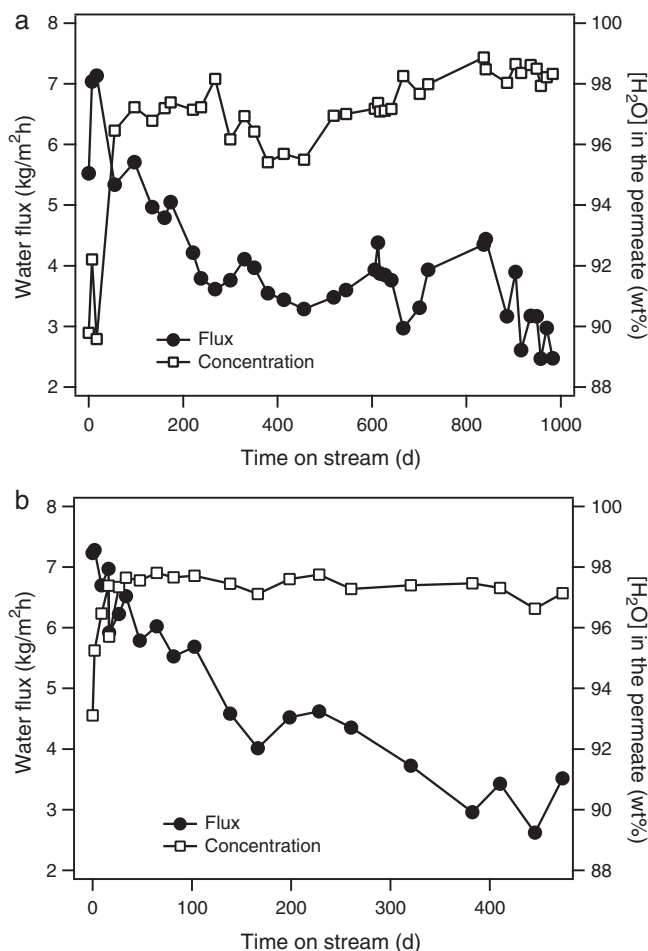


Fig. 4. Dehydration of 3 wt.% water in *n*-butanol at 150 °C by BTESE/MTES membranes, batch set up (a) and continuous setup (b).

an increase in the water vapor pressure from 1.7 bar in the previous experiment to 4.5 bar here. The water flux showed some fluctuation around ~5 kg/m² h, and was somewhat lower than would be expected on the basis of the results at 150 °C shown above. The difference can be ascribed to a somewhat thicker membrane layer for this specific membrane sample. The permeate contained about 99 wt.% water during the full testing period of 36 days. Remark-

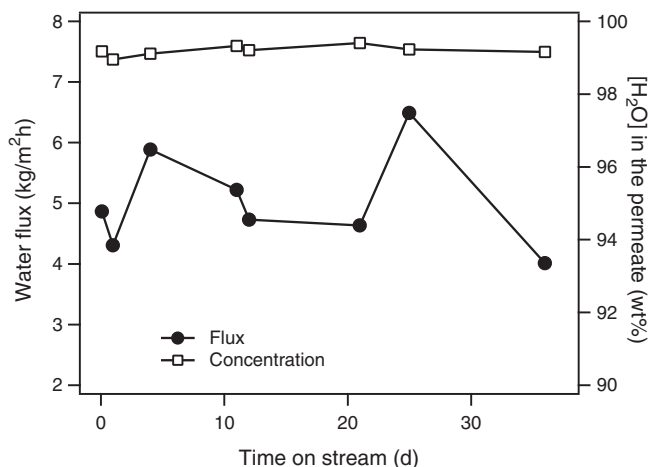


Fig. 5. Dehydration of 3 wt.% water in *n*-butanol at 190 °C by a BTESE/MTES membrane.

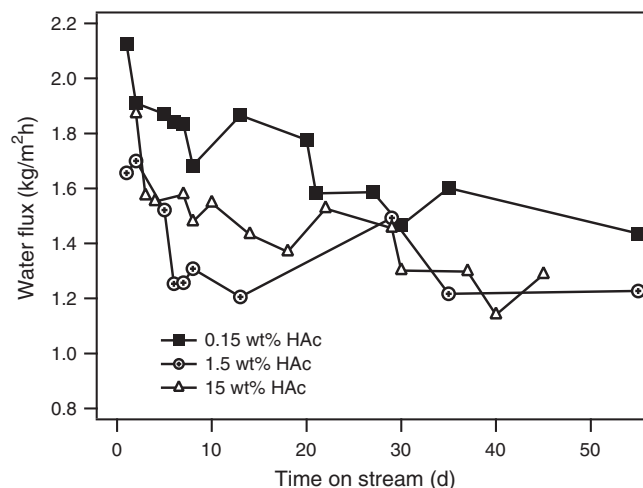


Fig. 6. Dehydration of 5 wt.% water in ethanol and 0.15, 1.5 and 15 wt.% HAC at 70 °C by a BTESE membrane.

ably, no initial flux decline and selectivity increase were observed. It is clear that the HybSi[®] membrane is suitable for dehydration pervaporation at temperatures up to at least 190 °C.

3.2.2. Influence of the presence of acetic acid

In bioethanol mixtures that leave the first distillation column, traces of organic acids can be present. To study their influence on the membrane performance and stability, mixtures of ethanol/water/acetic acid were used in dewatering tests on a BTESE membrane. Feed mixtures containing 5 wt.% water in ethanol and 0.15, 1.5 or 15 wt.% acetic acid were dewatered at 70 °C (Fig. 6). These concentrations correspond to a pH of 3.3, 2.8, and 2.3, respectively. The lower two concentrations and a parallel measurement without acetic acid were also reported elsewhere [15]. Two membranes were used and the membrane that was first tested in 0.15 wt.% acetic acid was transferred to the 15 wt.% mixture and testing with this membrane was continued for another 45 days. For all three mixtures reported here, the initial water flux was ~1.9 kg/m² h and decreased as a function of time; strongly during the first days and then more gradually. In all cases, the permeate contained over 85 wt.% water, which remained constant during the about 50 days of testing. The HybSi[®] membrane can clearly withstand mixtures including acetic acid during longer periods of time.

To test the influence of acids over a longer period of time than presented above, 1.5 wt.% of acetic acid was added to a feed mixture of 5 wt.% water in ethanol. This new membrane test was performed at 70 °C on a fresh BTESE membrane. An initial flux decline during the first ~20 days is followed by a fairly constant behavior (Fig. 7). The permeate contains about 85 wt.% of water and about 0.2 wt.% of acid over the 350 day period of continuous testing, showing the stability of the HybSi[®] membrane based on BTESE in acidified water–ethanol mixtures. The performance of this HybSi[®] membrane is comparable to the membrane presented in Fig. 6.

A high temperature (130 °C) stability test of a BTESE membrane in the presence of 1 wt.% of acetic acid was carried out for a mixture of 5 wt.% water in ethylene glycol (Fig. 8). Ethylene glycol was chosen because of its higher boiling point, which allows measurements at 130 °C without using a pressurized system. The flux decline during the first 10 days was stronger than in the previous experiments, and was accompanied with an increased concentration of water in the permeate. After this initial period both the flux and the selectivity stabilized. The separation of water from ethylene glycol with pervaporation is rather peculiar as also non-selective membranes can lead to a high separation factors under water lean conditions

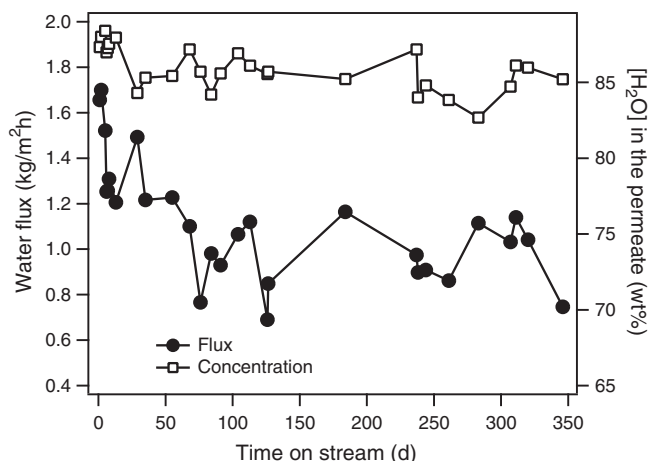


Fig. 7. Dehydration of 5 wt.% water in ethanol and 1.5 wt.% HAc at 70 °C by a BTESM membrane.

[22]. This was ascribed to the formation of a layer consisting of strongly absorbed ethylene glycol molecules on the pore surface. The strong decrease on water flux in this experiment is likely to be related to this phenomenon.

3.2.3. Influence of nitric acid

The performance of hybrid silica membranes in the presence of a mineral acid, HNO_3 , was tested by using a mixture of 5 wt.% water in *n*-butanol and a BTESE membrane. At the start of the pervaporation test 0.005 wt.% HNO_3 was added to this mixture. After 8 days, the acid concentration was increased to 0.05 wt.% (Fig. 9, line A) and after 17 days to 0.5 wt.% (Fig. 9, line B). These concentrations correspond to a pH of 3.2, 2.2 and 1.2, respectively.

Even though a freshly prepared membrane was used, no initial flux decline was observed. The permeate contained >99 wt.% of water in the presence of 0.005 wt.% of acid. Once the acid concentration was increased to 0.5 wt.% a gradual but steady flux decline was observed with a concomitant gradual decrease of the water concentration in the permeate. After 120 days of testing the permeate contained about 60 wt.% of water. These data indicate that although the HybSi® membranes cannot be applied in the presence of 0.5 wt.% of HNO_3 , the maximum concentration of a strong acid seems to be at least ~0.05 wt.%. Longer term testing using acid concentrations between 0.05 wt.% and 0.5 wt.% are required to confirm this preliminary finding.

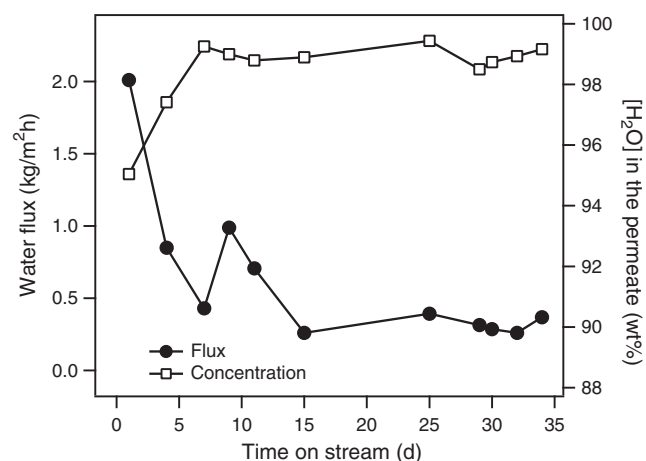


Fig. 8. Dehydration of 5 wt.% water in ethylene glycol and 1.5 wt.% HAc at 130 °C by a BTESM membrane.

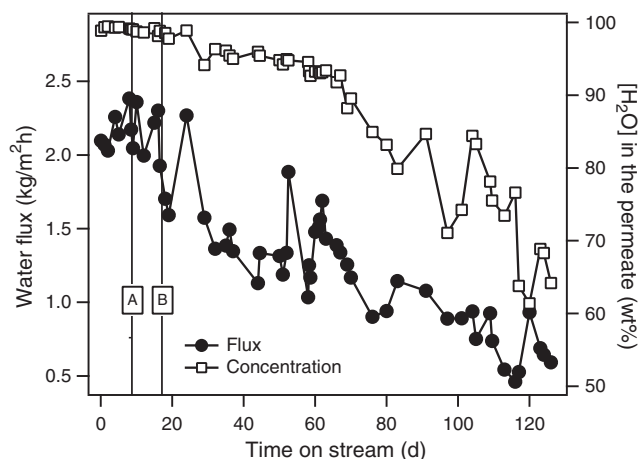


Fig. 9. Dehydration of 5 wt.% water in *n*-butanol and HNO_3 at 95 °C by a BTESE membrane, starting at 0.005 wt.% HNO_3 , increasing to 0.05 wt.% (line A) and 0.5 wt.% (line B).

3.2.4. Influence of methylsulfonic acid

A much more demanding acid stability test was performed on another BTESE membrane. After about 80 days of stable performance in the dehydration of *n*-butanol, 0.1 wt.% of methylsulfonic acid (MSA) was added (Fig. 10, line A) and a few days later the MSA concentration was increased to 1 wt.% (Fig. 10, line B). The values correspond to a pH in aqueous conditions of 2.1 and 1.1, respectively. MSA is a commonly used catalyst in esterification reactions. The addition of MSA led to a decrease of the water concentration in the permeate. Small amounts led to a decrease of the flux and large amounts to a strong increase (Fig. 10). Post-mortem analysis of the membrane reveals that both the $\gamma\text{-Al}_2\text{O}_3$ and hybrid silica layers were severely damaged and nearly removed from the surface of the support (Fig. 11). The membrane system was clearly not able to withstand these harsh conditions.

3.2.5. Dehydration of aprotic solvents

N-methyl pyrrolidone (NMP) is a frequently used solvent in the preparation of polymers. The stability of polymeric pervaporation membranes without specific treatment in this solvent is problematic, although some claims have been made that cross-linked polyimides are stable in NMP [23]. As the HybSi® membranes consist of both organic and inorganic constituents, dehydration measurements of NMP were performed as ultimate chemical stabil-

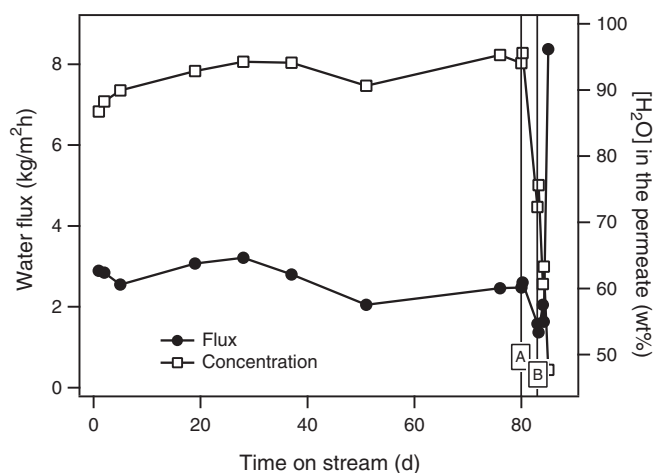


Fig. 10. Dehydration of 5 wt.% water in butanol and MSA at 95 °C by a BTESE membrane; addition of 0.1 wt.% MSA at 80 days (line A) and 1.0 wt.% at 83 days (line B) runtime.

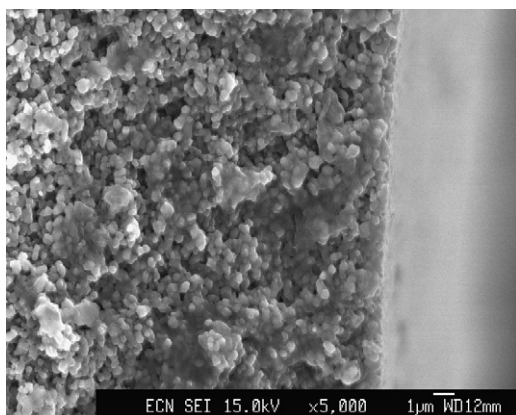


Fig. 11. Detailed SEM picture of the membrane after a pervaporation experiment with an MSA-containing feed.

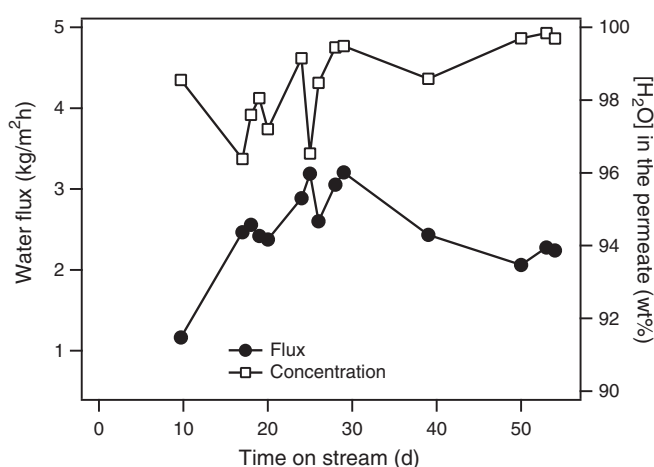


Fig. 12. Dehydration of 8 wt.% water in NMP at 130 °C, BTESE membrane.

ity test. NMP is one of the most aggressive aprotic solvents, and can be regarded as a representative example for the chemical stability of the membranes. During the first 10 days, the influence of feed concentration and temperature on the membrane performance has been tested using a BTESE membrane. Because of this the driving force in these tests changed and thus the fluxes changed. The data shown represent the measurements after stabilization of temperature and feed concentration. Over a period of 45 days the water flux was stable and the water concentration in the permeate increased gradually to >99 wt.% at 8 wt.% water in the feed and 130 °C (Fig. 12). From these data can be concluded that the membrane is stable in the dehydration of NMP.

Sommer [11,24] has shown that amorphous silica can be used for several aggressive solvents, including methylethylketone, dimethylformamide, acetonitrile (CH₃CN) and tetrahydrofuran. In our hands, HybSi® performed evenly well in the dehydration of these solvents, with the additional benefit of being stable at higher temperatures than both inorganic silica and methylated silica [21]. These measurements were done for a short period of time (1 day).

3.3. Discussion

3.3.1. High temperature stability

Constant performance for the dehydration of organic solvents under pervaporation conditions has been achieved with HybSi® membranes. During an initial period of several days the fluxes decreased and selectivity often increased. In the dehydration of *n*-butanol at 150 °C, the membrane was still very selective after

1000 days of continuous testing. Under the same measurement conditions, a ceramic-supported polyimide membrane failed after 120 days of testing [25]. For zeolite A membranes, no long term pervaporation performance data have been reported in the open literature and testing is limited to several hours in vapor permeation at 145 °C [26].

The origin of the enhanced hydrothermal stability of the HybSi® membranes as compared to other silica-based membranes has been ascribed to the incorporation of organic linking groups [14–19]. Unlike the Si–O–Si bonds, the Si–C_mH_n–Si bridges are not sensitive to hydrolytic attack. An additional explanation may be found in the crack propagation energy of the organically bridged materials, which is much larger than that of pure silica [27]. Other more speculative explanations that have been suggested are a lower surface diffusion coefficient and solubility of the basic constituents of the HybSi® material, BTESE and BTESM than the TEOS monomer of inorganic silica [14–19].

3.3.2. General flux stability

The origin of the initial flux decline as function of time in the data presented above cannot be unequivocally explained. Similar behavior was observed for methylated silica [21], for zeolite membranes [28], and for silica–zirconia membranes [29]. Fouling is expected not to play a role in the current study, as high purity chemicals have been used in the tests. A possible explanation is competitive adsorption of the organic species in the mixtures, thereby slowing down water transport. This mechanism is similar as reported for zeolite T membranes [28]. The long periods that are required before stabilization of the flux may be taken as an indication that simple adsorption of species from the feed mixture cannot be the sole cause for the flux decline. Rather, changes in the surface groups of the membrane resulting from an adsorption process would cause such a gradual decline. Another explanation is the appearance of –OH groups, making the pore more hydrophilic but also decreasing the effective pore size [29]. An alternative explanation is that hydrolysis of the atomic bonds leads to restructuring of the membrane material. This has been observed for zeolite A membranes [30] and for methylated silica membranes [21]. However, this continuing process would lead to an irreversible decrease of membrane performance and ultimately to loss of selectivity [21]. This was not observed for these membranes even after prolonged measurement periods of up to almost three years at 150 °C and for 1 year in the presence of significant amounts of acetic acid. In acidified media the flux decline seems to be somewhat stronger than in neutral media. For strong acids a loss of porosity and reorganization of the structure is more likely to occur [31]. In the end, the accompanying mechanical stresses could lead to the formation of defects, and as a result an increase in flux and further loss of selectivity. This is likely the cause for the performance loss in the presence of 0.5 wt.% of HNO₃ and also in the presence of methylsulfonic acid (MSA).

Interestingly, the degree and rate of flux decline clearly vary between different tests. This indicates that the specific test conditions play a major role in the mechanism of flux decline. As an engineering approach to counter flux decline, the process feed temperature could be increased gradually in time. This would bring the flux back to the desired level, by compensating for the flux decline as observed using constant operating conditions.

3.3.3. Acid stability

The HybSi® membranes can be used in the dehydration of ethanol containing a weak acid (acetic acid, pK_a = 4.75). The performance is reproducible and the membrane has proven to be selective up to 350 days at a pH of 2.8. Also, the presence of acetic acid at higher temperatures up to 130 °C, does not harm the membrane. In contrast, even minor concentrations of acid deteriorate the functionality of zeolite A membranes within a

few hours [30]. Zeolite T membrane, and especially the fluoride modified version has been reported to be more resistant [28,32]. Standard unmodified zeolite T is less stable. Some PVA membranes are reported to be resistant against acetic acid [33], whereas polyimide (Matrimid) membranes suffer from plasticization and swelling [34].

As an upper limit for the pH stability range a value of ~ 8 can be taken [16]. The organic bridges in HybSi[®] do not provide sufficient protection against the well-known rapid attack of silica-based materials under alkaline conditions. Operation well below a pH value of 2 seriously limits the life time of the γ -alumina supported HybSi[®] membrane system. At comparable estimated pH values of about 2, the membrane loses its selectivity in MSA much faster than in HNO₃. This is attributed to the difference in pK_a value, being -2 for MSA and -1.3 for HNO₃. As a result we anticipate a higher concentration of H⁺ in the case of MSA in the mainly organic liquid. The presence of large amounts of MSA is also detrimental for the γ -alumina layer. Replacement of the γ -Al₂O₃ mesoporous support layer by a material with a higher acid resistance, such as titania or zirconia, may expand the application window in the more acidic region of the HybSi[®] membrane. Still, the application of hybrid silica membranes in homogenous acid-catalyzed reactions (e.g., esterifications) may be problematic. Importantly, recent experiments have shown that solid acid catalysts can be used effectively in the presence of HybSi[®] [35], providing a suitable alternative. Another alternative, not explored yet, is to use the HybSi[®] membrane in the less demanding option of vapor permeation.

3.3.4. Solvent stability

In general, ceramic membranes are considered to be solvent stable. For methylated silica membranes excellent solvent stability was indeed already reported [11,24]. Here, it is shown that the stability of the HybSi[®] membrane, consisting of an organic–inorganic hybrid material is not influenced by the solvent, including the aprotic solvent NMP. More specifically, no indications were found for membrane swelling as commonly observed for polymer materials in such solvents.

4. Conclusions

The test program of the current study was designed to determine the operation window and stability limits of HybSi[®] membranes. The long term stable performance of these membranes under various demanding pervaporation conditions is unprecedented in literature. We conclude that these pervaporation membranes are applicable:

- Up to temperatures of at least 190 °C.
- In the range $\sim 2 < \text{pH} < 8$.
- In the dehydration of demanding aprotic solvents including NMP.

To the best of our knowledge, no competing membrane concept has comparable stability as HybSi[®] membranes in the dehydration of liquids with a high industrial value. Utilization of the HybSi[®] membranes in the presence of high concentrations of strong acids, at pH < 2 , is not recommended.

The option to use these membranes at high temperatures is an important advantage. As higher temperatures lead to higher fluxes, the required membrane area is lowered leading to lower overall costs. The improved chemical stability leads to a broadened application window and can open up markets that have so far been inaccessible for pervaporation membranes.

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