

Article

Wetting Resistance of Commercial Membrane Distillation Membranes in Waste Streams Containing Surfactants and Oil

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Abstract: Water management is becoming increasingly challenging and several technologies, including membrane distillation (MD) are emerging. This technology is less affected by salinity compared to reverse osmosis and is able to treat brines up to saturation. The focus of MD research recently shifted from seawater desalination to industrial applications out of the scope of reverse osmosis. In many of these applications, surfactants or oil traces are present in the feed stream, lowering the surface tension and increasing the risk for membrane wetting. In this study, the technological boundaries of MD in the presence of surfactants are investigated using surface tension, contact angle and liquid entry pressure measurements together with lab-scale MD experiments to predict the wetting resistance of different membranes. Synthetic NaCl solutions mixed with sodium dodecyl sulfate (SDS) were used as feed solution. The limiting surfactant concentration was found to be dependent on the surface chemistry of the membrane, and increased with increasing hydrophobicity and oleophobicity. Additionally, a hexadecane/SDS emulsion was prepared with a composition simulating produced water, a waste stream in the oil and gas sector. When hexadecane is present in the emulsion, oleophobic membranes are able to resist wetting, whereas polytetrafluorethen (PTFE) is gradually wetted by the feed liquid.

Keywords: membrane distillation; wetting; sodium dodecyl sulfate; hexadecane

1. Introduction

Membrane distillation (MD) is a thermally-driven membrane separation process, mostly applied to separate salts from an aqueous solution. The process uses a hydrophobic membrane to retain the liquid phase, while vapor is transported through the microporous structure. In direct contact membrane distillation, the membrane can be considered a contactor between the process liquids and the vapor phase, enabling 100% retention of dissolved components. Critical for the process is that the membrane pores are not wetted by the process liquids. As with any thermal separation process, MD is considered less energy efficient than reverse osmosis [1]. However, unlike reverse osmosis, MD can be applied using low-grade waste heat, solar or geothermal energy, considerably reducing the energy costs [2]. Moreover, the process flux and salt retention are less affected by salinity of the

feed and therefore the process is able to operate properly up to saturation [3,4]. Recently, membrane distillation has been applied more and more for challenging water streams with a much higher load of contaminants compared to seawater desalination. Examples include reverse osmosis (RO) brines [5–7], industrial waste water [8,9] and produced water [10,11]. In many of the applications, the contaminants include a combination of less soluble salts, organic foulants or components lowering the surface tension of the process fluids. The occurrence of scaling and fouling of these contaminants can decrease the performance of the membrane [6,12–19]. Another less investigated phenomenon is membrane wetting, where despite the hydrophobicity and controlled pore size, liquid is able to penetrate into the membrane. The liquid entry pressure (LEP) indicates the minimum pressure difference over the membrane at which membrane wetting will occur and is given by [20]:

$$LEP = -\frac{2\gamma_L \cos \theta}{r_{\max}} \quad (1)$$

where γ_L is the surface tension of the liquid, θ the contact angle of the liquid with the surface and r_{\max} the maximum pore radius.

Multiple origins of membrane wetting are known. Different MD studies show that the reduced hydrophobicity (θ) due to membrane fouling is a possible cause of membrane wetting [21,22]. Furthermore, defects present in the membrane influence r_{\max} and therefore strongly affect the liquid entry pressure [23,24]. The main focus of this article is the presence of organics lowering the surface tension (γ_L) of the feed stream, which can cause wetting as well [20,25,26]. The effect of membrane wetting for a series of alcohols, organic acids and solvents was already investigated [20,25]. Different approaches were used to quantify the wetting resistance of a membrane towards the presence of an organic component:

The determination of the concentration and surface tension (γ_{pd}) at which a droplet wets the membrane (penetrating drop method) for each organic component.

Determination of the theoretical maximum allowable surface tension in the process (γ_{pc}) using [25]:

$$\gamma_{pc} = \gamma_{pd} + \frac{\Delta P \cdot r_{\max}}{2B} \quad (2)$$

Where ΔP is the pressure drop over the membrane, r_{\max} the maximum membrane pore size and B a geometric factor between 0 and 1, where 1 indicates a perfectly cylindrical pore.

Measurement of the liquid entry pressure occurs as a function of the liquid composition.

Whereas the effect of alcohols, organic acids and solvent on the wetting behavior is described in literature [20,25], the effect of surfactants and oil traces on the membrane distillation performance has been less studied. Lin et al. [26] observed membrane wetting of a 0.45 μm polytetrafluorethen (PTFE) membrane at a sodium dodecyl sulfate (SDS) concentration of 28 mg/L, while a chemically-modified omniphobic membrane was able to resist wetting up to 115 mg/L SDS. Wang et al. showed that a 1000 ppm crude oil mixture immediately wets a 0.45 μm polyvinylidene fluoride (PVDF) membrane [27], while 100 ppm mineral oil is shown to substantially wet the membrane after 21 h [28].

This study aims to improve the understanding of membrane wetting in the presence of surfactants and oil. A commonly used surfactant, sodium dodecyl sulfate, was used to investigate the effect on surface tension, contact angle and membrane wetting in membrane distillation. The validity of a simple methodology correlating the surface tension, contact angle and liquid entry pressure to membrane wetting in membrane distillation was investigated for different concentrations of sodium dodecyl sulfate. Moreover, different membranes were used to investigate the influence of surface chemistry. Finally, a standard oil-in-water emulsion was prepared and tested with MD. The composition simulates the composition of produced water, which is a common waste stream in the oil and gas production [29].

2. Materials and Methods

Three different microporous membranes were used in this study: PTFE (Tetratex, Donaldson Company Inc., Belgium, Leuven), polyethylene (PE) (Solupor[®], Lydall Inc., Rochester, NH, USA) and oleophobic polyethersulfone (PES) (Supor[®], Pall Corporation, New York, NY, USA). Sodium chloride (technical grade), Sodium dodecyl sulfate (SDS; 98%) and hexadecane (99%) and were purchased from Sigma Aldrich (Saint Louis, MO, USA).

Solutions with a concentration of 35 g/L sodium chloride and different concentrations of sodium dodecyl sulfate ranging from 10 to 150 mg/L were prepared under continuous stirring for 1 h. The oil-in-water emulsion was prepared with 2400 mg/L hexadecane, 240 mg/L sodium dodecyl sulfate and 10 g/L NaCl. The components were mixed and ultrasound was applied for 30 min to stabilize the suspension. For the oil-in-water emulsion, the size of the oil droplets was measured by a particle size analyzer (Nanosight NS500, Malvern Instruments Ltd., Malvern, UK) and was found in the range of 0.1–0.5 μm with an average particle diameter of 0.3 μm [29].

The surface tension of the liquids was measured using a Force Tensiometer K6 from Kruss GmbH (Hamburg, Germany). The contact angle of the membranes was measured with an OCA 15EC Contact Angle System of Dataphysics (Filderstadt, Germany) using the static sessile drop method. The critical surface tension of wetting was determined for the PES membrane by measuring the contact angles using a series of alkanes (from hexadecane to hexane). The surface tension of the liquid that first shows a contact angle below 90°, i.e., the liquid that wets the membrane is assumed as the critical surface tension. For PTFE and PE, literature values are used. The liquid entry pressure was determined as described by Khayet et al. [30]. The hydrostatic pressure was increased slowly by 0.1 bar each 30 s, until a flow was detected. The porosity was measured using helium pycnometry as described in [31]. The thickness was obtained by imaging the membrane cross-section using a cold field emission scanning electron microscope (SEM) type JSM6340F (JEOL, Tokyo, Japan) as described in [31]. The average and maximum pore size were measured using a Porolux[®] 1000, with Porefil as wetting liquid and the shape factor assumed to be 1 [31].

The direct contact membrane distillation (DCMD) experiments were carried out using the experimental setup described in [32]. The process scheme of the setup is visualized in Figure 1. The module had a membrane area of 0.0108 m² and 2 mm thick polypropylene (PP) spacers were used. The feed and permeate temperatures were kept constant at 60 and 45 °C, respectively, for each experiment. The flow velocity was 0.13 m/s at feed and permeate side. The first MD test included a stepwise increase of the concentration of SDS up to 150 mg/L. These experiments were run for 2 h at each concentration. Additionally, longer tests were performed using 150 mg/L SDS, where the flux was measured over three days.

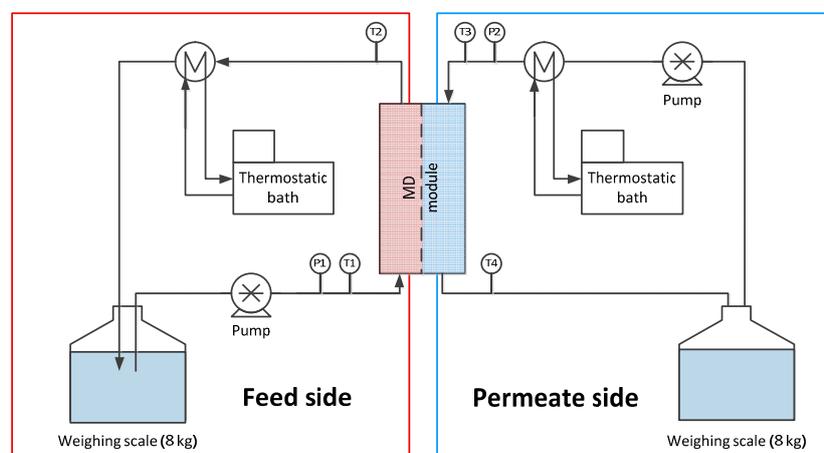


Figure 1. Process scheme of the direct contact membrane distillation (DCMD)-lab scale setup. T indicates a temperature sensor, P refers to pressure sensors.

3. Results

3.1. Membrane Characterization

The thickness (δ), porosity (ϵ) and mean pore size (d_{mean}) of the membranes used in this study is given in Table 1. These properties mainly determine the absolute flux [33]. The maximum pore size (d_{max}) and water contact angle (θ_{water}) are mostly important for the wetting resistance, which is sufficiently high for pure water. The water contact angle for the PTFE membrane is the highest (138°), followed by the PES membrane (132°) and the PE membrane (120°). The hexadecane contact angle ($\theta_{\text{hexadecane}}$) is used to test the oleophobicity of the membranes. As expected, PTFE and PE do not show any resistance to wetting of hexadecane, whereas the oleophobic PES membrane shows a contact angle of 92° with hexadecane.

Table 1. Properties of the membranes used in this study.

Membrane	δ (μm)	ϵ (%)	d_{mean} (μm)	d_{max} (μm)	θ_{water} ($^\circ$)	$\theta_{\text{hexadecane}}$ ($^\circ$)	LEP (bar)
PE	99	76%	0.30	0.43	138	0	3.9
PES	81	58%	0.51	0.59	132	92	4
PTFE	77	83%	0.17	0.19	120	0	10.8

3.2. Prediction of Membrane Wetting with Sodium Dodecyl Sulfate

3.2.1. Surface Tension

The surface tension of the aqueous solution of 35 g/L sodium chloride decreases with increasing concentrations of sodium dodecyl sulfate (SDS) (Figure 2). As described in the literature, the surface tension decreases strongly with increasing concentration of SDS up to 50 mg/L, after which an asymptotic level is reached at higher concentrations of sodium dodecyl sulfate [33–35]. This point correlates with the critical micelle concentration (CMC) of the surfactant. For pure water, the critical micelle concentration of 2560 g/L is reported for sodium dodecyl sulfate systems, whereas it is also observed that for salt-containing systems this value is much lower [35]. This means that salinity is an important aspect when studying the wetting behavior of a solution containing surfactants.

The critical surface tension for wetting, defined as the surface tension required to wet the membrane, is also indicated in the figure. Based on this figure, the PE membrane is expected to be wetted by the feed liquid if it contains 50 mg/L SDS or more. The surface energy of the PTFE and PES membranes is below the asymptotic value of the surface tension of the liquid up to 150 mg/L and therefore these membranes might be more suitable for treatment of surfactant containing waste streams.

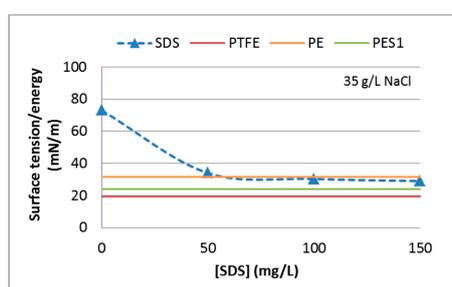


Figure 2. Surface tension as function of sodium dodecyl sulfate (SDS) concentration in an aqueous solution of 35 g/L NaCl and critical surface tension for the membrane surface used in this study.

3.2.2. Contact Angle

Figure 3 shows the contact angle of the three different membranes as a function of the sodium dodecyl sulfate concentration. The PTFE and PES membrane show contact angles above 90° for all SDS concentrations used in this study, whereas the contact angle with PE decreases below 90° for SDS

concentrations above 50 mg/L. Based on these results, wetting is only expected for the PE membrane at SDS concentrations higher than 50 mg/L, which confirms the observations in Section 3.2.1.

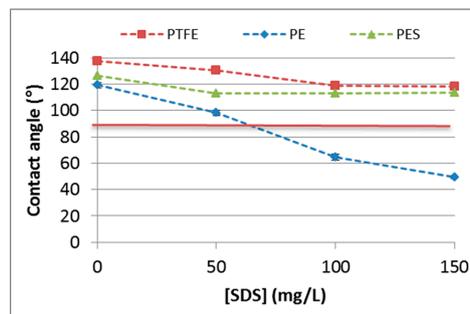


Figure 3. Contact angle measurements at different SDS concentrations, [NaCl] = 35 g/L.

3.2.3. Liquid Entry Pressure

Figure 4 presents the LEP for the three different membranes for a variety of SDS concentrations and 35 g/L NaCl. Up to a concentration of 50 mg/L SDS no immediate breakthrough of the liquid was observed for a pressure up to 4 bar for all three membranes. The maximum pressure of the experimental setup was 4 bar. Higher liquid entry pressures are therefore not measurable, which is indicated by the hatched bars. The PE and PES membrane shows a strong decline of LEP at higher SDS concentrations. However, in contrast to what was expected based on the surface tension and contact angle measurements, an LEP of 1.8 bar was still achieved at 150 mg/L SDS for the PE membrane. Neither the PES nor the PTFE membrane showed a severe decrease in contact angle and surface tension. Nevertheless, the lowest LEP of 1.4 bar at 150 mg/L SDS is observed for the PES membrane, while the PTFE membrane still shows a liquid entry pressure of 3.5 bar. This difference in behavior of the LEP is not expected based on the contact angle measurements, but can be explained due to a difference in pore size (Table 1), which is inversely correlated to liquid entry pressure (Equation (1)). The PES membrane has the highest maximum pore diameter of 0.59 μm , while the PTFE membrane has a maximum pore diameter of only 0.19 μm .

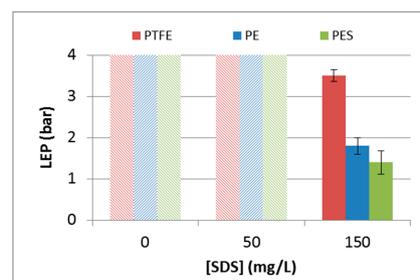


Figure 4. Liquid entry pressure at different SDS concentrations, [NaCl] = 35 g/L.

To measure the time dependence of the wetting an additional experiment was carried out. The membrane was placed inside the pressure cell and a constant pressure of 1 bar was applied, using a feed liquid of 150 mg/L SDS and 35 g/L NaCl. The pressure of 1 bar was selected based on the expected pressure drops in a full-scale MD module [36,37]. The PTFE membrane does not show any liquid penetrating the membrane after 30 min, whereas the PE and PES membranes show liquid breakthrough after 11 and 18 min, respectively. This shows that the liquid entry pressure measurements in Figure 4, with a pressure step of 0.1 bar each 30 s are not representative for long-term membrane operation in membrane distillation. The differences between the MD process and the liquid entry pressure tests might explain this behavior. A few wetted pores are only detected after sufficient time in the liquid entry measurement, while in MD an immediate increase of the permeate conductivity

is observed. In this respect, membrane distillation is much more sensitive in detection of leakages. The prediction of membrane wetting based on liquid entry pressure using this procedure might therefore be an underestimation and it is recommended that the time dependence must carefully be considered when evaluating the wetting behavior of a membrane.

3.2.4. Wetting Prediction

Based on surface tension and the water contact angle, no wetting is expected for the PTFE and PES membrane. The surface tension with a concentration of SDS of 50 mg/L decreases below the critical surface energy of PE. This is also visualized by the water contact angle, which decreases below 90° for concentrations above 50 mg/L SDS. Based on these two techniques, wetting in the MD tests is expected at a concentration of 50 mg/L SDS. In contrast, the liquid entry pressure for all membranes is above 1.4 bar, while at lab scale a pressure drop of 20 mbar is expected. This indicates that based on liquid entry measurement, no wetting is expected for the lab-scale MD tests. However, at a larger scale, MD pressure drop might increase up to 1 bar. The observation of leakage after applying a hydrostatic pressure difference of 1 bar on the membrane using 150 mg/L SDS points to possible membrane wetting in full scale modules for the PE and PES membrane.

3.3. Membrane Distillation with SDS

3.3.1. PE

Figure 5 shows the average flux and salt retention of the PE membrane using different SDS concentrations. Up to 40 mg/L, the flux is unchanged and the salt retention remains sufficiently high (>99.9%). At 50 mg/L SDS, the flux increases steadily over time. During the first hour of the experiment at 50 mg/L SDS, the flux was relatively stable, at $17 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, while the retention already decreased from 99.9% to 98.6%. These observations indicate wetting of a few membrane pores, enabling limited salt transport through the membrane. The fraction of dry membrane pores must be substantially high, because the flux is not affected and the salt retention remains above 98.6%. During the second hour of the experiment, the flux increased rapidly from $17 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ up to $40 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, while the retention decreased drastically from >98.6% to 69.5%, which indicates severe wetting of the PE membrane at these concentrations. The SDS concentration is not further increased above 50 mg/L, because even more severe wetting problems are expected. Based on the contact angle measurements, wetting would occur between 50 and 100 mg/L, while based on the LEP measurement, no wetting is expected up to 1000 mg/L. This shows that the contact angle and surface tension are more reliable measures for prediction of membrane wetting than the LEP. The short-term exposure LEP in Section 3.2.3 did not predict membrane wetting under these experimental condition, and is therefore found to be an unreliable measure for wetting prediction.

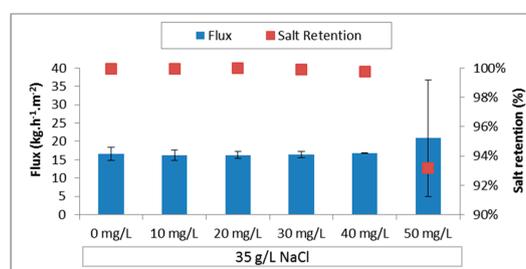


Figure 5. Flux and salt retention for the PE membrane for a feed composition with different SDS concentrations and 35 g/L NaCl.

3.3.2. PTFE

The same concentrations of SDS were used with the PTFE membrane. The fluxes and salt retentions for each concentration are given in Figure 6a. The PTFE membrane shows a stable performance over 2 h of operation up to an SDS concentration of 150 mg/L, as is expected based on the water contact angle and LEP measurements. Figure 6b shows the daily average flux and retention for the MD experiment with 150 mg/L SDS and 35 g/L NaCl. Despite the fact that a stable performance was observed for the short-term experiments over 2 h, longer-term experiments show the intolerance of PTFE membranes for surfactants. Partial pore wetting is gradually provoked by the surfactant and results in salt transport from feed to permeate.

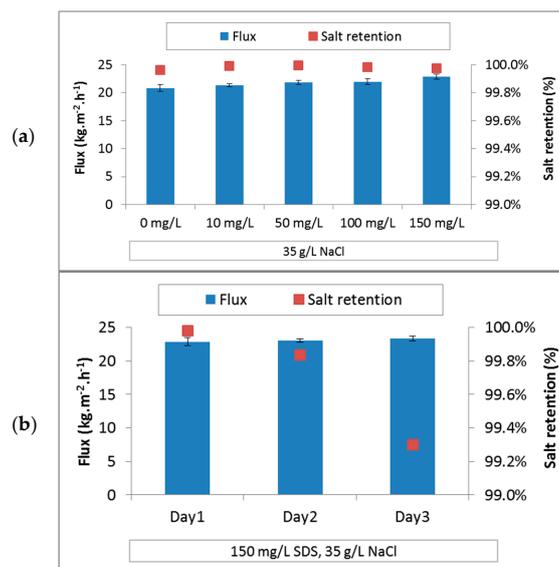


Figure 6. Flux and salt retention for the PTFE membrane; (a) with increasing SDS concentrations; (b) At constant feed composition over three days.

3.3.3. PES

In contrast to the PE and PTFE membrane, the flux and retention of the PES membrane did not indicate any wetting at the different SDS concentrations used in this study (Figure 7). In addition, a three-day test at the highest SDS concentration of 150 mg/L shows salt retention. This behavior is in accordance with the predictions based on the surface tension and the contact angle measurement. The liquid entry pressure of 1.4 bar at 150 mg/L SDS is sufficient for lab-scale testing, because in the lab setup, the pressure drop did not exceed 0.02 bar for the process conditions used in this study. Nevertheless, it is remarkable that the PES membrane showed a lower LEP compared to the PTFE membrane, while it does show a better salt retention during the MD-tests. As observed during the determination of the critical surface tension, the PES membrane does not wet using hexadecane, proving its oleophobic character. These tests show that this membrane feature can improve the performance of the membrane in terms of wetting resistance in the presence of surface-lowering components.

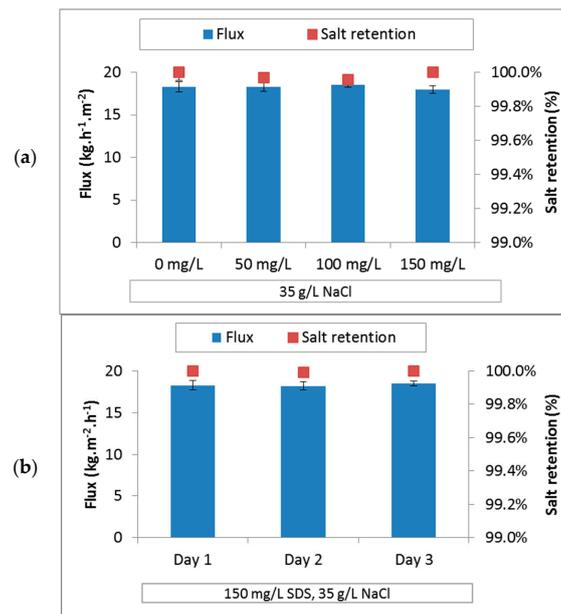


Figure 7. Flux and salt retention for the PES membrane, (a) with increasing SDS concentrations; (b) at constant feed composition over three days.

3.3.4. Summary

The best prediction for the immediate wetting in membrane distillation was obtained using the surface tension measurement combined with the contact angle of the fluid with the membrane. Based on this quick and easy measurement, a first estimation of the technical feasibility and a selection of the membrane can be made. However, long-term gradual wetting, as observed with the PTFE membrane, was not predicted by surface tension, contact angle or liquid entry pressure. In addition, when applying the liquid at 1 bar for a longer time (30 min) no wetting was observed, indicating that the long-term membrane wetting as observed in the PTFE membrane is more difficult to predict using quick analytic experiments.

3.4. Synthetic Produced Water

3.4.1. Prediction of Membrane Wetting

An emulsion of hexadecane in water was prepared to study the resistance of membrane against wetting in the presence of oily substances. The surface tension of the synthetic produced water was 47 mN/m, which is much higher compared to the lowest surface tension of the solutions with sodium dodecyl sulfate of ± 32 mN/m (Figure 2). It is expected that the sodium dodecyl sulfate forms micelles around the hexadecane, shielding the hexadecane from the air-liquid interface. The oleophobic tail emulsifies the oil, at the same time diminishing its capability of reducing the interfacial air-water surface tension (Figure 8). The contact angle of the synthetic produced water with PTFE and PES was 127°. Membrane wetting was therefore not expected for either membrane. Due to the severe wetting of the PE membrane observed during the SDS experiments, this membrane was not further considered for the treatment of oil emulsions.

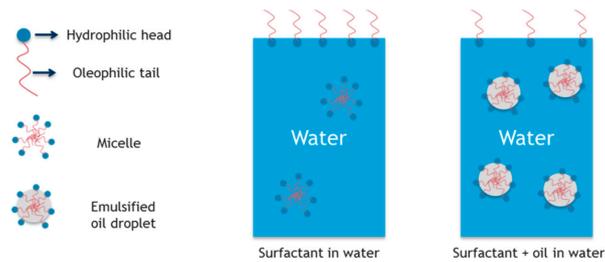


Figure 8. Micelle formation with surfactant in water mixture and emulsification of the oil-in-water mixture.

3.4.2. Membrane Distillation Testing

Figure 9 shows the flux of the PTFE and the PES membrane during a one-day test. The flux using the PTFE membrane was stable up to 4 h of operation. At that moment, water was added to the feed to keep the feed concentration constant. Thereafter, the flux decreases to zero. Figure 10 shows the visual transformation from opaque to transparent of the PTFE membrane, which shows the gradual wetting during the course of the experiment. Remarkably, no increase was observed in permeate conductivity for the PTFE, which remained below 20 $\mu\text{S}/\text{cm}$. When refilling the feed vessel with water, the emulsion is locally broken (observed visually) and hexadecane is able to penetrate the membrane. Since the hexadecane and PTFE are both apolar molecules, the membrane takes up the hexadecane, which remains in the membrane and blocks the flux. Sodium chloride is not soluble in hexadecane, explaining the unexpected combination of flux decrease due to membrane wetting, without loss of salt retention. In contrast to PTFE, the flux of the PES membrane only steadily decreases, with only 9%. No visual observation of wetting was observed for this membrane, however the steady decrease might indicate that some of the pores are also blocked by the hexadecane, reducing the flux, causing the slight decrease in flux.

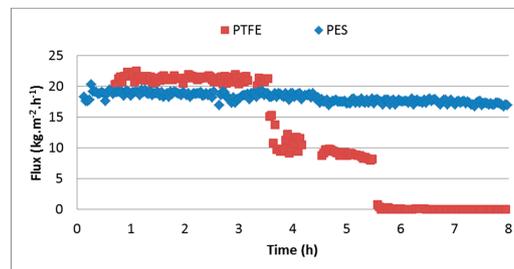


Figure 9. Flux as function of time for PTFE and PES with the oil/SDS mixture as feed solution.

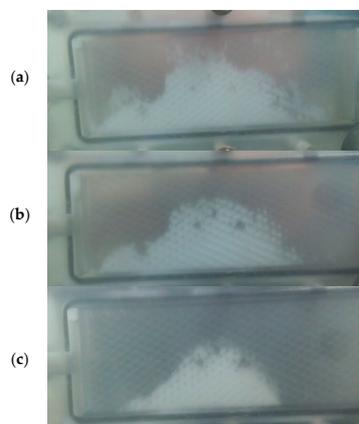


Figure 10. Pictures of the PTFE membrane during the experiment with oil/SDS mixture after (a) 4 h; (b) 5 h; (c) 6 h of MD operation.

4. Conclusions

In this manuscript it was shown that immediate wetting in membrane distillation can be predicted by surface tension and water contact angle measurements. The surface tension measurement shows that wetting behavior might not only depend on sodium dodecyl concentration, but also on the NaCl concentration, which strongly affects the critical micelle concentration. The PE membrane is less hydrophobic compared to PTFE and is therefore more susceptible towards membrane wetting due to the presence of surfactants. This membrane shows immediate wetting, a severe salt increase in the permeate, and a flux increase induced by the hydrostatic pressure difference. For PTFE the short-term test did not show changes in salt retention for SDS concentrations far above the critical micelle concentration (SDS: 150 mg/L, NaCl: 35 g/L). However, three-day MD testing shows that despite the sufficiently high contact angle with the PTFE-membrane, a decrease of the salt retention is observed, while still maintaining stable fluxes. This shows that the wetting is much less severe compared to the PE membrane, but that at longer operational times membrane wetting might also become an important issue. The PES membrane is oleophobic and showed unaffected flux or salt retention over three days of testing. Additionally, membrane distillation experiments with synthetic produced water showed the better stability in performance of an oleophobic membrane compared to a hydrophobic PTFE membrane.

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