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Fouling of polyelectrolyte multilayer based nanofiltration membranes during produced water treatment: The role of surfactant size and chemistry
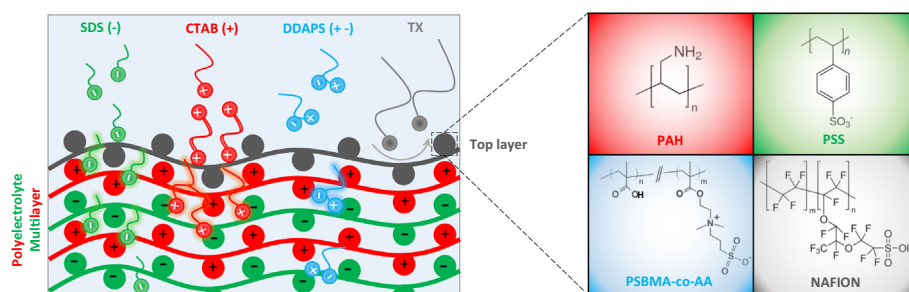
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Large volumes of water become contaminated with hydrocarbons, surfactants, salts and other chemical agents during Oil & Gas exploration activities, resulting in a complex wastewater stream known as produced water (PW). Nanofiltration (NF) membranes are a promising alternative for the treatment of PW to facilitate its re-use. Unfortunately, membrane fouling still represents a major obstacle. In the present work, we investigate the effect of surface chemistry on fouling of NF membranes based on polyelectrolyte multilayers (PEM), during the treatment of artificial produced water. To this end, oil-in-water (O/W) emulsions stabilized with four different surfactants (anionic, cationic, zwitterionic and non-ionic) were treated with PEM-based NF membranes having the same multilayer, but different top layer polymer chemistry: crosslinked poly(allylamine hydrochloride) (PAH, nearly uncharged), poly(sodium 4-styrene sulfonate) (PSS, strongly negative), poly(sulfobetaine methacrylate-co-acrylic acid) (PSBMA-co-AA, zwitterionic) and Nafion (negative and hydrophobic). First, we study the adsorption of the four surfactants for the four different surfaces on model interfaces. Second, we study fouling by artificial produced water stabilized by the same surfactants on PEM-based hollow fiber NF membranes characterized by the same multilayer of our model surfaces. Third, we study fouling of the same surfactants solution but without oil. Very high oil retention (>99%) was observed when filtering all the O/W emulsions, while the physicochemical interactions between the multilayer and the surfactants determined the extent of fouling as well as the surfactant retention. Unexpectedly, our results show that fouling of PEM-based NF membranes, during PW treatment, is mainly due to membrane active layer fouling caused by surfactant uptake inside of the PEM coating, rather than due to cake layer formation. Indeed, it is not the surface chemistry of the membrane that determines the extent of fouling, but the surfactant interaction with the bulk of the PEM. A denser multilayer, that would stop these molecules, would benefit PW treatment

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by decreasing fouling issues, as would the use of slightly more bulky surfactants that cannot penetrate the PEM.

1. Introduction

One of the main environmental challenges in the Oil & Gas (O&G) field is the sustainable management of produced water (PW). This wastewater consists of water already present in the drilled geological formation together with an aqueous solution of chemical agents that is injected into the formation during the hydrocarbon recovery process [1]. PW is the largest waste stream formed during oil and gas recovery, representing in some cases more than 90% of the O&G liquid waste [2]. The volume of PW generated is expected to increase further in the future due to the growing share of hydrocarbons that are recovered using water-intensive methods. Moreover, as older O&G fields get depleted, larger volumes of injected water will be required to extract the remaining resources [3].

PW can be considered an oil-in-water (O/W) emulsion in which different molecules (corrosion inhibitors, biocides and extraction enhancers) act as surfactants, stabilizing the oily-phase and keeping it dispersed [4]. The amount and type of compounds present in PW will differ depending on the well from which the hydrocarbons are extracted, as well as on the chemical agents added to the water during the recovery process. After treatment, PW could be re-injected to extract further resources, reducing the freshwater demand of the O&G industry. Ideally, if higher quality standards are met, treated PW could also be reused in other sectors such as agriculture, livestock raising and industrial processes [2].

Conventional treatment of PW mainly includes physical processes, as for example adsorption, media filtration and cyclones, and chemical methods, such as de-emulsification and chemical precipitation [5]. Even though it is possible to remove most of the contaminants present in PW by a combination of conventional treatment methods, these processes often involve the use of large volumes of chemical agents, require a large installation space and can be energy-intensive [6]. Consequently, the development of novel, energy and resource-efficient technologies is needed to ensure that treated PW complies with increasingly strict water quality standards for its reuse [7].

Over the past decades, researchers have shown the potential of membranes to effectively treat O/W emulsions [8,9]. Although conventional physical, chemical and biological treatment processes can remove free-floating oil as well as oil present in unstable emulsions, these methods are not sufficiently effective in separating well-stabilized emulsified oil droplets from water, mainly due to their small size (<10 μm) and high stability [9,10]. Membranes, ranging from microfiltration (MF) to nanofiltration (NF), have been proven to be extremely effective in the removal of such small and stable droplets, providing higher quality effluents with a series of advantages in terms of environmental impacts, space requirements and easy to automate operation when compared to traditional methods [11]. Here, NF membranes have an array of added advantages as they can be used at acceptable permeability for de-oiling while simultaneously removing multivalent ions, dissolved organics and part of the monovalent salts [12,13], providing higher quality effluents than MF and ultrafiltration (UF) with lower use of energy than reverse osmosis (RO).

Several studies have obtained promising results for the use of NF in PW treatment. Muppalla et al. tested the performance of a NF membrane prepared by applying a pentablock copolymer (PBC) active layer on top of a polysulphone UF membrane and obtained high oil rejection (~99.5%) from oil-water emulsions [14]. Xu & Drewes observed high permeability, salt and total organic content (TOC) removal when treating PW with commercially available NF membranes on a bench-scale [15], while Visvanathan et al., after conducting a pilot-scale experiment, concluded that NF was a suitable option for the pre-treatment of PW before applying a reverse osmosis (RO) step, thanks to its stable efficiency and low-fouling performance [16]. Besides, Alzahrani & Mohammad reviewed the application of membrane technologies, including NF, for the treatment of PW [12]. Despite the favorable outcomes, previously mentioned, they stressed the need of considering NF as part of a PW treatment train, consisting of several steps. The complexity of PW makes single-step solutions impossible [5], especially if the quality of the effluent is expected to meet strict beneficial reuse standards. Further research and development is required on several aspects of NF application [17], including the important topic of membrane fouling [4,18].

Fouling is a major drawback common to all filtration technologies, leading to a decrease in permeate quantity and quality over time, which in turn translates into lost operation periods and higher costs due to membrane cleaning or even replacement [19]. Several of the organic compounds present in PW, such as oil, dissolved organics and surfactants, can easily lead to fouling [12,10]. Physicochemical interactions between organic molecules and membrane surface lead to adsorption, which is considered the main mechanism for organic membrane fouling [20]. Surfactants are a type of organic foulant that requires special attention in the case of PW treatment by NF since they are responsible for the stability of the emulsion and can interact in several ways with the membrane [4]. While the extent of fouling for charged surfactants is mainly related to electrostatic interactions [21], for non-ionic surfactants it seems to be related to the membrane hydrophilicity and pore size [22]. Researchers have therefore suggested that in order to minimize fouling it is recommended to use membranes with a more hydrophilic, smoother surface, and same charge as the fouling agents [23,24]. As membrane charge and surface chemistry are believed to be the main parameters able to affect fouling [25], a zwitterionic top layer could prevent fouling by decreasing the interaction between membrane surface and foulants [26]. However, the role of membrane charge and surfactant chemistry remains still unclear, especially in PW treatment, and needs further investigation.

In the past decade, we have seen a major breakthrough in the production of polyelectrolyte multilayer (PEM) based hollow fiber (HF) nanofiltration membranes. The excellent separation properties of these systems, coupled with very good chemical stability, has led to many publications [17,27–30], but also to very rapid commercialization [31]. Additionally, PEM-based NF membranes have a key advantage over commonly used thin film composite (TFC) NF membranes. As TFC membranes are still commercially available only as flat sheets, as it is quite difficult to make TFC membranes via IP in a hollow fiber configuration [32]. Here, our PEM based membranes have the advantage that hollow fiber manufacturing is very straightforward and HF-based membrane modules do not require a spacer, in contrast to spiral wound modules, where spacer fouling is a much bigger problem than membrane fouling [33]. However, a rather unexplored area of PEM based membranes is their fouling behavior. This is worth mentioning since the chemistry of these systems very naturally

lends itself to a large deal of control over the membrane surface chemistry [34–36]. As such, PEM based HF membranes could easily be designed with good separation properties, combined with anti-fouling properties optimized towards PW treatment.

In this manuscript, we study the effect of top layer polymer chemistry, as well as surfactant type, on fouling by PW for PEM-based nanofiltration membranes. As surface chemistry is believed to be the main factor that regulates the interactions between membrane and foulants, it is ideal to investigate such effects on PEM, where we can create very similar membrane active layers, and apply a different top layer to change the membrane surface chemistry. First, we focus on surfactant adsorption on PEM coated model interfaces to investigate the effect of different top layer polymer chemistry (nearly uncharged crosslinked poly(allylamine hydrochloride) (PAH), strongly negative poly(sodium 4-styrene sulfonate) (PSS), zwitterionic poly(sulfobetaine methacrylate-co-acrylic acid) (PSBMA-co-AA) and negative hydrophobic Nafion) on the adsoption of four different surfactants (anionic SDS, cationic CTAB, zwitterionic DDAPS and nonionic TX). Subsequently, we study fouling by artificial PW (prepared with various surfactants) on NF membranes having the same multilayer chemistry of the model interfaces. The same experiments are also carried out with aqueous solutions of just the surfactant to better understand the underlying fouling mechanisms. While we expected the top layer chemistry to play a major role in membrane fouling by surfactants, our experiments surprisingly demonstrate that it is not the top layer chemistry that determines the degree of fouling, but rather the surfactant size and type and their interaction with the inner part of the PEM. These results indicate clear pathways to reduce fouling of PEM based NF membranes during PW treatment.

2. Materials and methods

2.1. Chemicals

O/W emulsions were prepared by mixing N-hexadecane (Merck Schuchardt 99.0%) in a solution containing one out of four surfactants, namely sodium dodecyl sulfate (SDS, Sigma-Aldrich, ACS reagent, 99.0%), hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich, for molecular biology, 99%), Ndodecyl-N, N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS, Sigma-Aldrich, 97.0% (dried material, CHN)) and Triton^{TM} X-100 (TX, Sigma-Aldrich, laboratory grade). Fig. 1 shows the chemical structure of the surfactants used in this work as well as their molecular weight (MW, Da).

PEM-based NF membranes were prepared by coating sulfonated poly(ether sulfone) (SPES) UF-HF membranes (inner diameter of 0.7 mm, molecular weight cut-off (MWCO) of 7.5 kDa, and water permeability of 150 LMH/bar [13]) with four types of polyelectrolytes: PAH (Mw = 50 kDa), PSS (Mw = 70 kDa), Nafion (75wt.% of 1100 EW Nafion) and PSBMA-co-AA. All of the polyelectrolytes used for membrane coating were purchased from Sigma Aldrich except for PSBMA-co-AA, which was synthetized by following the procedure described by de Grooth et al. [37]. Using ^{1}H NMR (spectra reported in Figure S1, Supporting Information, SI), the monomer distribution of PSBMA-co-AA was estimated to be approximately 10:1 M ratio of SBMA/AA. For the crosslinking of the PEM, a 25% aqueous solution of glutaraldehyde was purchased from Sigma-Aldrich. Coumarin 6/ Neeliglow Yellow 196 (Neelikon) fluorescent dye was used to measure oil content by means of fluorometry. Silicon wafers were purchased from WaferNet Inc. (San Jose, CA, USA). We purchased all other chemicals from VWR, the Netherlands. All chemicals were used without further purification steps.

2.2. Model surface coating with PEM

Polyelectrolyte coating solutions were prepared by dissolving 0.1 g/L polyelectrolyte in a 50 mM NaCl solution without adjusting pH (with pH~5.5). All the steps (coating, rinsing and crosslinking) step were performed at room temperature and each of them lasted 15 min. First, negatively charged Silica (SiO$_2$) wafers were cleaned with piranha solution (3:1 mixture of concentrated sulfuric acid (H$_2$SO$_4$) with hydrogen peroxide (H$_2$O$_2$)) to remove possible organic contaminants. Then, the wafers were dipped in a polycation (PAH) solution (50 mM NaCl) and subsequently rinsed with an aqueous solution containing only NaCl (50 mM). The model interfaces were then immersed in a polyanion (PSS) solution (50 mM NaCl), followed by another rinsing step, to finally complete the fist bilayer. A crosslinking step, in which the model surfaces were immersed in a 7.5 mM glutaraldehyde solution (50 mM NaCl), was applied after coating each PAH layer to guarantee layer stability in surfactant solutions [13]. The procedure was repeated until 4.5 and 5 bilayers, respectively for PAH and the other top layers (i.e. negative PSS, zwitterionic PSBMA-co-AA and negative hydrophobic Nafion), were coated on top of the wafers. While PSS and PSBMA-co-AA coating solutions contained 50 mM NaCl
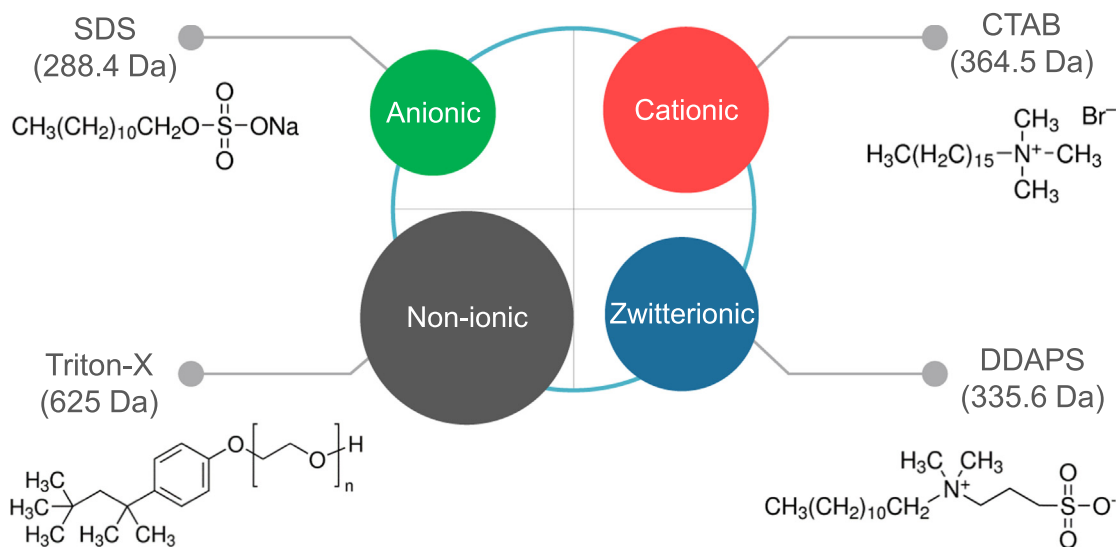

Fig. 1. Surfactants tested in this work and their characteristics: anionic SDS (288.4 Da), cationic CTAB (364.5 Da), nonionic TX (625 Da) and zwitterionic DDAPS (335.6 Da).

and 0.1 g·L^{-1} of the respective polyelectrolyte, the Nafion coating solution consisted of 0.1 g·L^{-1} Nafion dispersed in ethanol 70%. The same coating procedure is applied on hollow fiber membranes (Section 2.4).

2.3. Surfactant adsorption on model interfaces via reflectometry

PW can be considered an oil-in-water emulsion in which different molecules (corrosion inhibitors, biocides and extraction enhancers) act as surfactants, stabilizing the oily-phase and keeping it dispersed. Surfactants are a type of organic foulant that requires special attention in the case of PW treatment by NF since they are responsible for the stability of the emulsion and can adsorb at the membrane interface [21,38].

We initially investigated the adsorption of four different surfactants on model interfaces via reflectometry [39]. To quantify the adsorbed amount of surfactant at the interface, we flushed the surfactant solutions (0.1 times the critical micelle concentration (CMC) of the surfactant and 100 mM NaCl) to the silica wafers, previously coated with PEMs (above described). For simplicity we have taken the CMC value in absence of salt, being aware that especially for the charged surfactants the CMC will decrease at higher salinities. When we reach steady state in surfactant adsorption, we rinse our interfaces with a simple salt solution (100 mM NaCl). The use of a stagnation point flow cell allows to study the surfactant adsorption under well controlled hydrodynamic conditions. We calculate the amount of surfactant, Γ (mg/m^2), adsorbed on the model interface as follows

$$\Gamma = \frac{\Delta S}{S_0} Q, \tag{1}$$

where ΔS is the change in the ratio (S (–)) between the two polarized components originated from the reflection and splitting of the monochromatic light (HeNe laser, 632.8 nm) used in the system, S_0 is the initial output signal of the model interface (–), and Q is the sensitivity factor (mg/m^2). The last parameter (Q) is calculated by using an optical model based on the following system parameters: θ = 71°, n_{SiO_2} = 1.46, $\tilde{n}_{Si}$ = (3.85, 0.02), n_{H_2O} = 1.33, δ_{SiO_2} = 90 nm and refractive index increment dn/dc (mL/g) for every surfactant (reported in Table 1). The refractive index increment of DDAPS was calculated after measuring the refractive index (at 20 °C and 590 nm) of different DDAPS solutions (50, 500, 1000, 5000, 10000, 50000 mg/L) with an ATR-BR Schmidt Haensch refractometer. We calculate and report the sensitivity factor Q for each surfactant in Table 1. We performed all experiments at least in duplicate.

2.4. Membrane coating and characterization

The UF support membranes were coated following the same procedure adopted for the model surfaces (Section 2.2). Initially we coated the UF membranes with one PAH-PSS bilayer by submerging the fibers in a solution (50 mM NaCl) containing 0.1 g·L^{-1} PAH, then moving them into a rinsing solution (50 mM NaCl) and finally into a solution (50 mM NaCl) with 0.1 g·L^{-1} PSS. Three additional bilayers were added to the membrane by repeating this process, including crosslinking steps in which the membranes

were immersed, after adding each PAH layer, in a 7.5 mM glutaraldehyde solution with 50 mM NaCl. Once the first four PAH-PSS bilayers were added to the fibers, an additional PAH coating was performed followed by a final crosslinking step. After this, the membranes were split into four groups. One of these groups was not coated any further, leaving it with a 4.5 bilayer PEM terminated with a PAH top layer. The other three groups were each coated with a different top layer, namely PSS, PSBMA-co-AA and Nafion, for a total of 5 bilayers. For the case of PSS and PSBMA-co-AA, the coating solutions contained 50 mM NaCl and 0.1 g·L^{-1} of the respective polyelectrolyte, while the Nafion coating solution consisted of 0.1 g·L^{-1} Nafion dispersed in ethanol 70%. Every step (coating, rinsing and crosslinking) lasted 15 min and was carried out at room temperature. After all the desired layers were coated, the membranes were rinsed in demineralized water, and then stored for 4 h in a glycerol-water solution (15/85 wt%). Finally, the membrane fibers were left to dry overnight at room temperature. We refer from this point onwards to the coated membranes according to their terminating layer, namely PAH, PSS, PZWT (PSBMA-co-AA) and NAF (Nafion). Individual modules were prepared by assembling single PEM-coated fibers into transparent plastic tubes of 8 mm diameter and approximately 170 mm length. For the evaluation of the membranes permeability, the clean water flux (CWF) was determined by pumping demineralized water through the fibers in a cross-flow configuration for 1 h, at room temperature and constant transmembrane pressure (TMP) of 3 bar. The cross-flow velocity through the fibers was maintained at approximately 1.7 m·s^{-1} (Reynolds number around 1200) in order to minimize the effects of concentration polarization. Fig. 2 shows a schematic of the experimental set-up used in this study. Water permeability was then calculated in terms of LMH/bar with the measured CWF and TMP values (Figure S2, SI). All our PEM-based NF membranes have a negative zeta potential. Specifically, we find the zeta potentials for PAH, PSS, PSBMA-co-AA and Nafion polymer coatings to be respectively −10.9, −22.9, −25.8 and −14.6 mV (Figure S3, SI). Ion retention was determined by performing 1-h crossflow experiments, at the same TMP and temperature conditions as water permeability experiments, with 5 mM solutions of four different salts: NaCl, CaCl$_2$, Na$_2$SO$_4$ and MgSO$_4$. The results are reported in Figure S4 (SI).

Conductivity was measured in the feed and permeate samples using a Mettler Toledo SevenExcellence^{TM} pH/Conductivity meter.
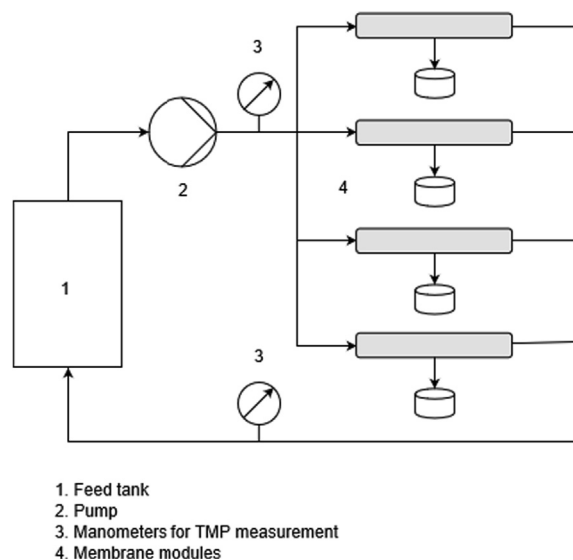
Table 1
Refractive index increments (dn/dc) and sensitivity factors for the surfactant solutions.

Surfactant	dn/dc (mL/g)	Q (mg/m^2)
SDS	0.108 [40]	45
CTAB	0.150 [40]	35
DDAPS	0.146	30
TX	0.154 [41]	30

1. Feed tank
2. Pump
3. Manometers for TMP measurement
4. Membrane modules

Fig. 2. Schematic of the experimental set-up for membrane filtration experiments.

Ion retention was calculated based on the obtained data as a ratio between conductivity measured in the permeate samples and the feed solution. Since the concentrate outflow was recirculated into the feed solution while permeate volumes were collected as samples, the conductivity of the feed was measured before and after the ion retention experiments in order to detect changes in the feed composition. These changes in feed composition were negligible since the collected permeate volume was much smaller than the total feed volume. Four fibers were tested in every experiment to obtain at least a triplicate set of results for each set of experiments.

2.5. Artificial Produced Water preparation and filtration

Fouling experiments were performed on PEM-coated fibers using O/W emulsions (artificial PW) prepared by mixing 1 g·L^{-1} of N-hexadecane in a solution containing 100 mM NaCl and an amount of surfactant equivalent to 1/10 of its critical micelle concentration at 0 salt (CMC), which corresponds to 34.6 mg/L for CTAB, 239.1 mg/L for SDS, 100.6 mg/L for DDAPS and 14.4 mg/L for Triton-X. Each emulsion contained only one type of surfactant. The procedure followed to prepare the artificial PW was the same as described in previous works [13,42,43]. In order to measure oil retention, N-hexadecane was first energetically mixed with the fluorescent dye in 15 mL sample tubes. The resulting mixture was then filtered through a Millipore 0.45 μm filter to remove any solid residuals. The dyed oil was then injected with a long syringe needle into a 1L Schott-Duran bottle in a solution containing 100 mM NaCl and 1/10 CMC of surfactant, and mixed using a IKA® T25 digital Ultra-Turrax® with S25N 18G element for 10 min at 14000 rpm. In this work no zeta potentials were obtained for the emulsions. For similar surfactant concentrations and ionic strength, O/W emulsions are known to be strongly negatively charged for SDS (zeta potentials of −110 to −120 mV [44,45]), strongly positively charged for CTAB (∼+85 mV [45,46]), slightly negative for TX (from −20 to −5 mV [47]) and negatively charged for DDAPS (from −35 to −45 mV [48]).

Before each fouling experiment, the water permeability of clean membranes was measured as described in Section 2.4. Afterwards, the residual water remaining in the tested modules was removed and the same cross-flow configuration was used to run the fouling experiments with artificial PW. Pressure and temperature conditions were kept the same as during the water permeability tests (3 bar TMP and room temperature), while the flow velocity was set to 0.43 m·s^{-1} (Reynolds number ∼300) to enhance fouling. The artificial PW was treated by the membranes for 3 h. Permeate volumes were collected from each fiber after the first 2 h of the experiment to estimate permeate flux in terms of LMH/bar. After running each fouling experiment, pH of the filtered PW was measured using a Mettler Toledo SevenExcellence™ pH/Conductivity meter. The fibers were then rinsed by running a solution containing 100 mM NaCl and the respective 1/10 CMC of surfactant, same concentrations of the artificial PW but without oil. The rinsing step lasted 15 min and was performed without applied pressure at 1.7 m·s^{-1} crossflow velocity. Finally, the water permeability through the fiber was measured to assess the residual fouling. The ratio between the permeability measured during PW filtration and the initial clean water permeability was used to estimate the flux decline due to irreversible and reversible fouling. We refer to the ratio between the water permeability after cleaning and water permeability for clean membrane (before fouling experiments) as "flux recovery". This term is an indication of the extent of irreversible fouling on the fibers.

The feed and permeate composition during the filtration of PW were analyzed in terms of ion retention and TOC content by means of ion chromatography (Metrohm Compact IC 761) and a TOC analyzer (Shimadzu TOC-L), respectively. Oil retention was determined by using a Perkin Elmer Victor3™ V 1420 Multilabel Counter spectrophotometer to measure the fluorescence of different dilutions of the feed solution with known oil concentration. Given that the artificial PW used in the experiments contains two main fouling agents, namely oil droplets and surfactant molecules, additional fouling experiments were conducted by running solutions containing 1/10 CMC of surfactant and 100 mM NaCl without oil to show the relative contribution of free surfactants to membrane fouling. The fouling tests with these surfactant solutions were performed under the same conditions as the ones performed with PW, with no flushing step and 30 min experiment instead of 2 h. Indeed, while fouling by oil-in-water emulsions for NF membranes can take up to few hours to reach steady-state [49], in our experiments we noticed that, for PEM-based NF membrane, fouling by surfactants is a fast process, reaching already the steady state in 30 min. Flux ratio and flux recovery after fouling were also measured for all top layers and surfactants in the same way as in the fouling experiments with O/W emulsions. In order to assess the extent of fouling due to the adsorption of oil droplets, we compared flux recovery measured after fouling with PW with the results after fouling with surfactant solutions. For each type of surfactant and top layer, the difference between the average flux recovery after filtering surfactant solutions and PW is an indicator of the flux decrease related to oil adhesion on the membrane.

3. Results and discussion

The Results and Discussion of this manuscript is divided into three major sections. In the first section, we investigate the adsorption of different surfactants (i.e. anionic, cationic, zwitterionic and nonionic) on model interfaces coated with the same PEM but with different top layer charge and chemistry. In the second section, we study fouling from simple surfactant solutions and from the corresponding artificial PWs on HF membranes coated with same PEM. Based on the results from both sections we finally discuss the expected fouling mechanisms, with a focus on the role of surfactant size and chemistry.

3.1. Surfactant adsorption on model interfaces

Membrane fouling during the filtration of O/W emulsions, such as PW, is highly affected by the chemistry and charge of the surfactant that stabilizes the emulsion [42,43,50–52]. Surfactants do not only affect fouling by giving charge and stability to the oil droplets of the emulsion but additionally adsorb at the membrane surface [21,38].

The adsorption of surfactant at the membrane surface is expected to be influenced by both membrane surface chemistry and charge, as well as by multilayer composition. In order to study the interactions that take place at the feed-membrane interface, here we investigated the adsorption of the four different surfactants (anionic SDS, cationic CTAB, zwitterionic DDAPS and nonionic TX) on model PEM surfaces.

Optical reflectometry allowed us to study the adsorption of surfactant on model interfaces, previously prepared with same multilayer ((PAH/PSS)$_{4.5}$), but terminating with four different polymer chemistries. Even if the water content, and therefore water permeability, of PEM can change according to the applied top layer [53], chemical crosslinking allowed for very similar multilayers with similar water permeability (see Figure S2, SI). Every model interface was flushed with a surfactant solution until its adsorption reached steady state. The steady state value represents the total amount of surfactant adsorbed on the PEM. We also evaluated

the fraction of reversible (and irreversible) adsorption, for each surfactant, by flushing the coated model interfaces with a rinsing solution having same pH and salinity of the surfactant solution. We report the irreversibility of surfactant adsorption on model interfaces in the Supporting Information (Table S1, SI).

Fig. 3 shows the adsorption of the four surfactants on multilayer coated with different polymer chemistry (nearly uncharged crosslinked PAH, negatively charged PSS, hydrophobic Nafion and zwitterionic PSBMA-co-AA). However, changes caused by concentration polarization that can occur in the vicinity of the membrane surface during filtration are not taken into account by Fig. 3. As a consequence, changes in steady-state adsorption values may occur during filtration, as shown by our adsorption isotherms (see Fig. S5, SI).

On all our PEM model surfaces, we observed relatively high adsorption values (2–2.5 mg/m^2) for the cationic CTAB. This is in agreement with literature, as the adsorption of CTAB on negative surfaces, with formation of a monolayer or bilayer, has been widely corroborated [54,55]. CTAB is positively charged while all the multilayers we investigated have a net negative charge mainly due to chemical crosslinking (via GA) [56]. The observed behavior is thus due to electrostatic interaction, responsible at first for CTAB adsorption, but also hydrophobic interactions, which lead to attraction between the hydrophobic surfactant tails and the formation of surfactant micelles or a bilayer on top of the negative surface [55]. Slightly lower values of adsorption are observed for PSBMA-co-AA surfaces [57–59]. A reduced amount of DDAPS (∼0.5 mg/^{2}) adsorbed on PAH, Nafion and PSBMA-co-AA surfaces but not on PSS. This is an unexpected result as DDAPS was previously found to interact more with anionic moieties rather than cationic moieities, similarly to nonionic surfactants containing polyoxyetylene units, such as TX [60]. As expected, TX adsorbed on PSS and Nafion, which are more negatively charged than PAH, with almost no adsorption observed for PAH and PSBMA-co-AA top layers [24].

Differently, SDS in our studies adsorbed on all the top layers and, in some cases (like for PAH and PSS), partially removed the multilayer from the substrate, as we can observe from the negative

values. This is in agreement with our previous study [13]. If this phenomenon occurs also on membranes, we should notice worse performances and higher water and salt permeability during filtration (see Section 3.2 for further details).

3.2. Membrane fouling during produced water treatment

As already mentioned, surfactants play a crucial role in membrane fouling not only because they adsorb at the membrane surface but also because they stabilize the oil droplets of PW, determining this way the charge of the stabilized droplets.

In the previous section, we studied surfactant adsorption on model interfaces via reflectometry, but membrane fouling is certainly not only determined by surface adsorption. In this section, we investigate fouling by monitoring the flux decline of our membranes during filtration. The procedure is carefully described in Section 2.5. Sodium chloride, TOC and n-hexadecane (oil) retention are measured in each of the experiments. In all the cases, NaCl retention was found 5–15%, oil retention > 99% and the pH did not change during filtration.

3.2.1. Fouling of crosslinked PAH terminated membranes

In Fig. 4, we show the normalized flux for nearly uncharged PAH membranes after fouling with O/W emulsion and only surfactant solutions. The degree of fouling is clearly affected by the surfactant used in the emulsion or solution filtrated. In particular, the magnitude of fouling follows the order SDS > CTAB > DDAPS > TX.

Although for negatively charged membranes one might not expect fouling by anionic surfactants [21], the presence of a multilayer makes this more complex. Anionic surfactants were previously found to easily complex with the cationic polyelectrolyte (PAH) of the multilayer [61,13], and this effect could lead to the observed fouling.

On the other side, the cationic CTAB also induces a relevant flux decline, probably due to the fact that CTAB can easily complex with the anionic polyelectrolyte (PSS) and adsorb inside the multilayer (see Fig. 3). DDAPS and TX, probably due to their charge and size
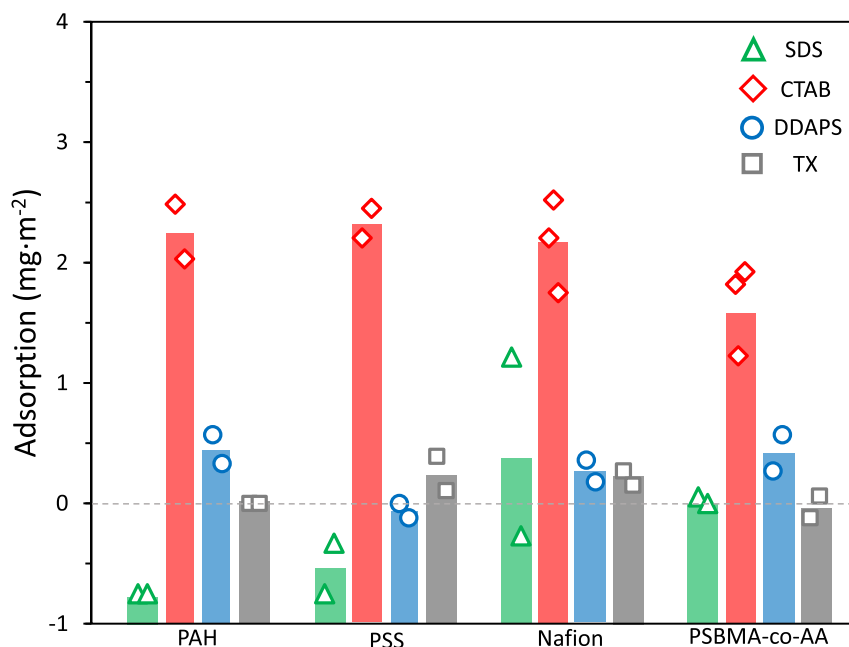

Fig. 3. Adsorption (mg/m^2) of surfactants on model surfaces coated with PAH, PSS, Nafion and PSBMA-co-AA top layers. Results obtained via reflectometry. Points represent single data points, while bars represent the average of these points. Negative values correspond to multilayer desorption caused by surfactant complexation. All the experiments were performed at least in duplicate, as shown.
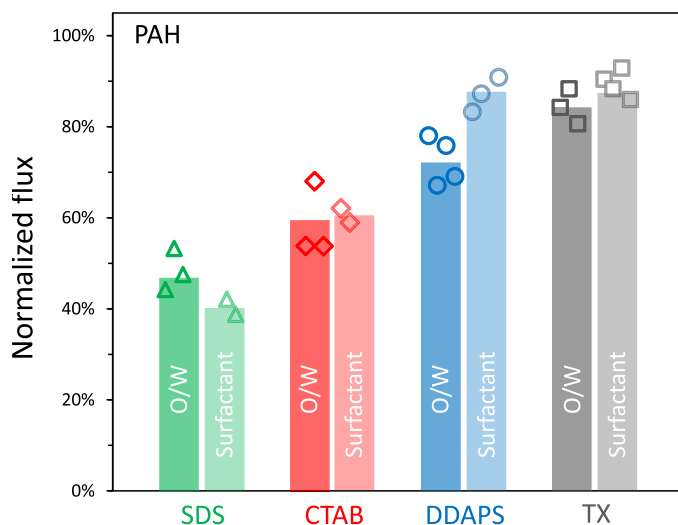
Fig. 4. Normalized membrane flux of PAH membranes after fouling with O/W emulsions (dark columns) and surfactant solutions (light columns) stabilized by different surfactants (SDS, CTAB, DDAPS and TX). O/W emulsions were made of 100 mM NaCl, 1000 mg/L of n-hexadecane (oil) and surfactant at 1/10 CMC (239.1 mg/L for SDS, 34.6 mg/L for CTAB, 100.6 mg/L for DDAPS and 14.4 mg/L for TX). Surfactant solutions had same salt and surfactant composition of O/W emulsions but did not contain oil. Marks represent single data points while bars their average. All the experiments were performed at least in triplicate, as shown.

respectively, foul less, in agreement with our adsorption studies (see Fig. 3).

3.2.2. Fouling of PSS, PSBMA-co-AA and Nafion terminated membranes

Fig. 5 shows the normalized flux for negative PSS, zwitterionic PSBMA-co-AA (PZWT) and negative hydrophobic Nafion terminated membranes after fouling with O/W emulsion and only surfactant solutions. The results are quite surprising, as for all surface chemistries, the degree of fouling is determined mainly by the surfactant used in the emulsion or solution filtrated, with SDS > CTAB > DDAPS > TX. If the membranes surface chemistry would be responsible for foulant-membrane interactions, we should have expected big differences between the four top layers. But, fouling follows the same trends for all the top layers with only small differences between them. The only differences we can actually attribute to the different top layer chemistry are the ones we do see in absolute values.

In our previous work, we studied the fouling of PEM based membranes with three similar surface chemistries with relevance to surface water treatment [26]. For the tested foulants, including BSA, LUDOX, Lysozyme, humic acids and alginates, a very clear

effect of membrane surface chemistry was observed. In that case especially the zwitterionic surfaces were demonstrated to be very low-fouling [26]. So why is such an effect not observed for the fouling of artificial produced water as studied here? The key difference lays on the size of the foulants that here seems to completely dominate the fouling behaviour. Surfactants molecules are much smaller and cannot just adsorb on top of the PEM, but also inside of it.

3.3. Effect of surfactant size and chemistry on PEM membrane fouling

As mentioned in the previous section, surfactant chemistry and size seem to be determinant in multilayer fouling. It has been observed in the filtration of pharmaceuticals that NF membranes with bigger pore size suffer more from fouling [62]. Adsorption plays an important role in pore blocking, especially when the pores of the membrane are already restricted due to adsorption of a foulant which is small enough to penetrate into the pores (pore narrowing) [19]. In this case, the size of the surfactant plays a crucial role. Surfactants, especially SDS and CTAB, can easily diffuse in the $(PAH/PSS)^{4.5}$ multilayer and even adsorb in it.

Interestingly, surfactants are typically used as model foulants for ion exchange (IEX) membranes [63–65]. In those systems it is well established that negative surfactant molecules can bind to positively charged sites in an anion exchange membrane (AEM), thereby replacing the anionic counter-ion such as Cl^- or OH^-. The adsorbed surfactants densify the membrane and block transport pathways, leading to reduced membrane performance.

Our results demonstrate that surfactant fouling is a big issue also for PEM based NF membranes. This fits well with the internal chemistry of the PEM separation layers. Similarly to IEX membranes described above, the PEM separation layers will contain charged moieties bound to an oppositely charged counter-ion (extrinsically compensated charges [66]). But in contrast to the IEX membranes, the PEM separation layer will contain both anionic and cationic charges. In particular, anionic SDS and cationic CTAB were the surfactants that fouled the most, independently of the chemistry of the outer layer. If surfactants are small enough to diffuse in the multilayer, they can locally adsorb, by complexing with the free charges in the PEM layer, densifying the layer and increasing the resistance to water permeation.

3.3.1. To the roots of PEM based NF membranes fouling during filtration of PW

Even if cake layer build-up is typically considered one of the main causes of membrane fouling, especially for PW treatment, our work shows that for these NF membrane internal multilayer fouling is dominant. In this context, Figs. 4,5 allow us to discriminate between multilayer fouling and cake layer fouling. The first, as
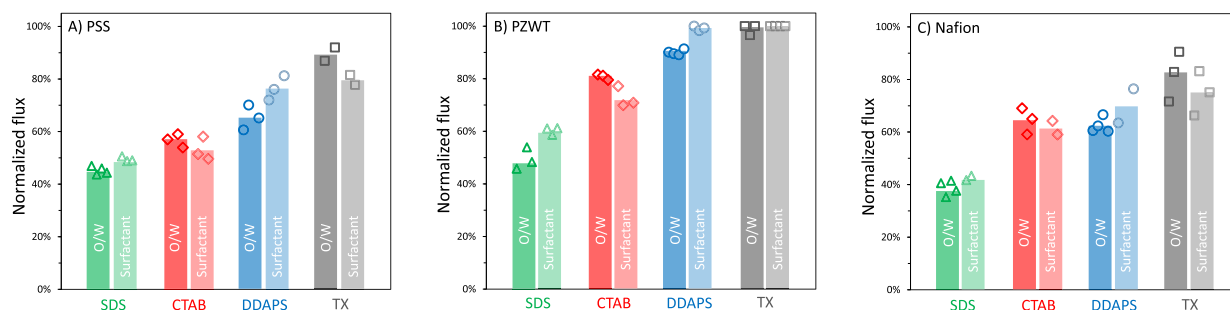

Fig. 5. Normalized membrane flux of membranes with A) PSS, B) PZWT and C) Nafion top layers after fouling with O/W emulsions (dark columns) and surfactant solutions (light columns) stabilized by different surfactants (SDS, CTAB, DDAPS and TX). O/W emulsions were made of 100 mM NaCl, 1000 mg/L of n-hexadecane (oil) and surfactant at 1/10 CMC (239.1 mg/L for SDS, 34.6 mg/L for CTAB, 100.6 mg/L for DDAPS and 14.4 mg/L for TX). Surfactant solutions had same salt and surfactant composition of O/W emulsions but did not contain oil. Marks represent single data points while bars their average. All the experiments were performed at least in triplicate, as shown.
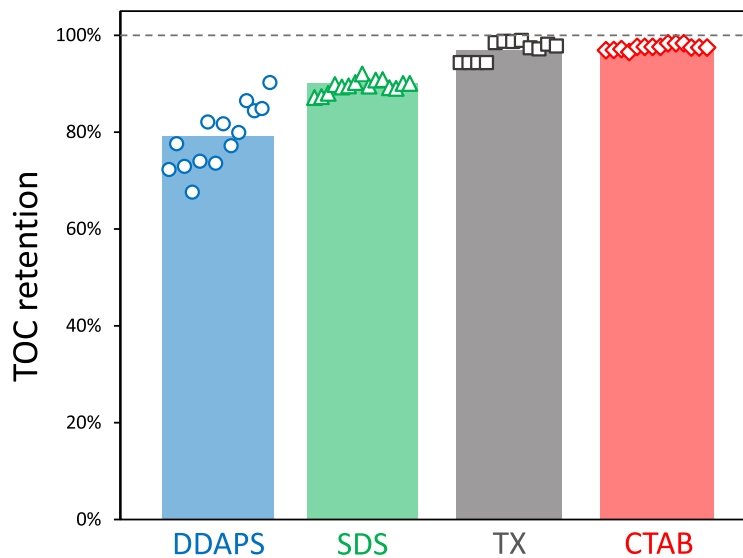
Fig. 6. TOC retention of PEM hollow fiber (nearly uncharged PAH, negatively PSS, zwitterionic PSBMA-co-AA and negatively hydrophobic Nafion) membranes during experiments with O/W emulsions stabilized by DDAPS, SDS, TX and CTAB. Marks represent single data points while bars their average.
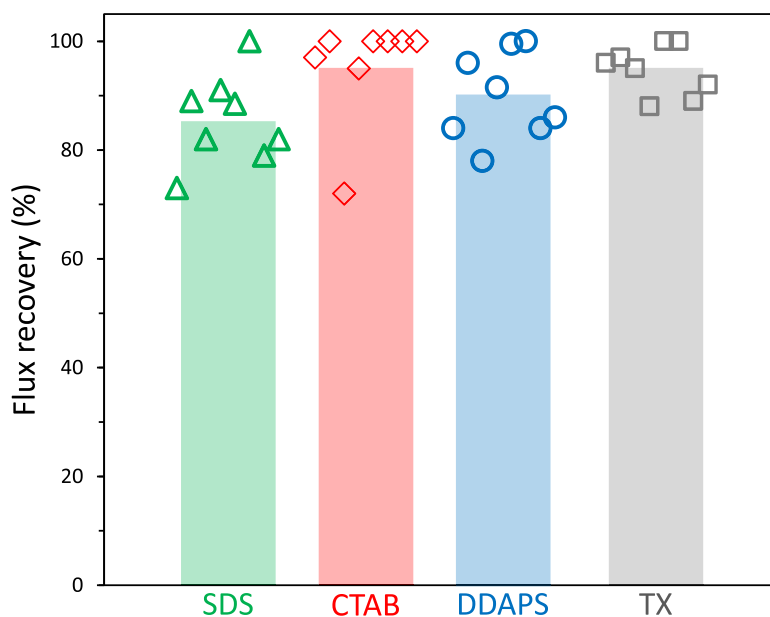

Fig. 7. Average of flux recovery (%) of nearly uncharged PAH, negatively PSS, zwitterionic PSBMA-co-AA and negatively hydrophobic Nafion membranes for every different set of fouling experiments (with O/W emulsions and only surfactant solutions for SDS, CTAB, DDAPS and TX). Single data points values and SD are reported in tables S6-S7.
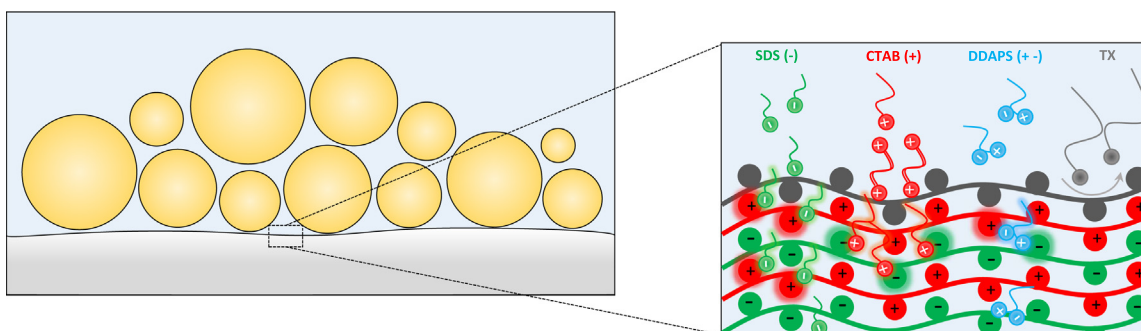

Fig. 8. Illustration of NF fouling by surfactant stabilized oil-in-water emulsions.

mentioned above, can be mainly attributed to surfactant adsorption in the membrane active layer, which causes increased resistance to the water transport. The second, is due to the build-up of a cake layer of oil droplets on top of the membrane surface [4]. While we should be able to see both effects of fouling when filtering O/W emulsions, we see only multilayer fouling when filtering surfactant solution. The contribution of the cake layer resistance should therefore be observed in the difference between normalized flux due to fouling by surfactant solutions and fouling by O/W emulsions. The cake layer resistance is generally low for TX, while quite relevant for DDAPS. On the other side, for SDS and CTAB we do observe more fouling when filtering only surfactant, which could appear unexpected. Here, the build-up of a cake layer on top of the membrane could slow down, via electrostatic repulsion, the diffusion of SDS and CTAB molecules into the membrane. Moreover, the free surfactant concentration in the oil-in-water emulsion may be lower, as many surfactant molecules are bound to the oil-water interface.

One may think that if the retention of salt during filtration drastically increases due to the layer densification caused by the surfactant interaction with the multilayer, we could observe a reduced flux because of an increased osmotic pressure at the membrane interface and therefore misinterpret fouling. However, we did observe low rejection of NaCl retention during O/W emulsion filtration and report these values in tables S2-S5 of SI.

Fig. 6 shows the TOC retention of our PEM membranes for the different surfactants tested. The observed retention values (lower than 100%) demonstrate that our surfactants can indeed penetrate the multilayer. Two factors, the size of the surfactant and its specific interaction with the multilayer, are expected to affect their retention during filtration as well their fouling behaviour. Previously, Fig. 3 showed that cationic CTAB and anionic SDS interact the most with the multilayer, and Figs. 4,5 showed that they foul it the most. Contrarily, DDAPS and TX interact less with the multilayer and even foul it less. On the other hand, smaller surfactants (SDS (288.4 Da) < DDAPS (335.6 Da) < CTAB (364.5 Da) < TX (625 Da)) are expected to diffuse easier through the multilayer.

In Fig. 7 we show the flux recovery for both experiments, with and without oil, in presence of surfactant for all our membranes. High flux recoveries are found, as would be expected if the surfactant adsorption indeed dominates the fouling, since surfactant adsorption is highly reversible. We can conclude that fouling was mostly reversible for all the solutions tested.

From our results, we can easily conclude that fouling is highly affected by not only specific interactions but also size of the surfactant. While TX gave the most severe fouling issues in UF [42], in NF it is the surfactant that fouls the least as, due to its size, it cannot easily penetrate into the membrane to cause internal fouling. In addition, in contrast with recent interpretations from literature findings [49], in NF, cake layer fouling is not found to be a big issue. The oil droplet cake layer is likely so open that the main resistance to water permeation stems from the PEM separation layer, especially when densified by internal uptake of surfactants. The fouling of our PEM base NF membranes is schematically illustrated in Fig. 8.

SDS is the smallest surfactant, and its negative charge can easily interact with free cationic groups in the PEM. For that reason, it is SDS that fouls our PEM membranes the most. DDAPS has a slightly lower size than CTAB, but it does not give extremely high fouling issues in our filtration experiments, as the zwitterionic surfactant interacts less strongly with internal charges of the PEM. At steady-state, CTAB hardly permeates into the PEM separation layer, probably because of its strong interaction with free anionic groups which could cause a significant layer densification. Finally, the uncharged and largest surfactant, TX, hardly fouls the membrane as it does not permeate into it and lacks interaction with the inter-

nal charges. These observations provide clear directions on how to improve PEM based NF membranes for the treatment of PW. For example, a denser multilayer would be beneficial for PW treatment, as it could stop even the smallest surfactant molecules, preventing the possibility of internal fouling. Another opportunity is to select more bulky and uncharged surfactant molecules such as TX for enhanced oil recovery and more bulky cationic surfactants as corrosion inhibitors to further decrease the negative impact of fouling.

4. Conclusions

The sustainable management of produced water is one of the main environmental challenges in the Oil & Gas field. Membrane technology can tackle such a challenge, but fouling still remains a major issue and its causes are not yet well understood. In this work, we highlight surfactants as the dominant fouling species when treating produced water with PEM based NF membranes. We prepared HF NF membranes based on PEMs and studied membrane fouling by only surfactant as well as the corresponding O/W emulsions. Our membranes exhibited high oil retention (>99%), while the physico-chemical interactions between the multilayer and the surfactants determined the extent of fouling, as well as the surfactant retention. While surfactants in MF and UF mainly affect fouling by conferring chemistry to the oil cake-layer, our results prove that in PEM based NF surfactant adsorption into the active layer should be considered as the main cause of fouling in PW treatment. In addition, while we expected different top layers applied on top of the same multilayer to show a different fouling behaviour, it was instead really similar, clearly indicating that for small molecules such as SDS, CTAB and DDAPS, it is not the outer layer chemistry that determines the extent of fouling but the active layer, i.e. the internal multilayer, chemistry. A denser multilayer [67,68], able to stop these surfactant molecules, would highly benefit PW treatment by decreasing fouling issues of NF membrane modules, while allowing de-oiling and organic molecules removal in one-step process. Alternatively, the use of larger, and preferentially uncharged, surfactant molecules [69], or even polymers [70,71], in enhanced oil recovery would also substantially reduce the impact on membrane fouling. Finally, as the presence of surfactants can affect the rejection of divalent ions [13], future research should also focus on the interplay between surfactants and divalent ions in membrane fouling and ions retention.

CRediT authorship contribution statement

Ettore Virga: Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing - original draft, Visualization, Supervision, Project administration. **Mario Alejandro Parra:** Validation, Investigation, Data curation, Visualization. **Wiebe M. de Vos:** Conceptualization, Writing - review & editing, Visualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

Appendix A. Supplementary material

^{1}H NMR of PSBMA-co-AA, membranes permeability, zeta-potential measurements for the coated HF membranes, salts retention, and irreversibility and isotherms of surfactant adsorption, ions and oil retention during filtration of artificial PW. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2021.02.119.

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