

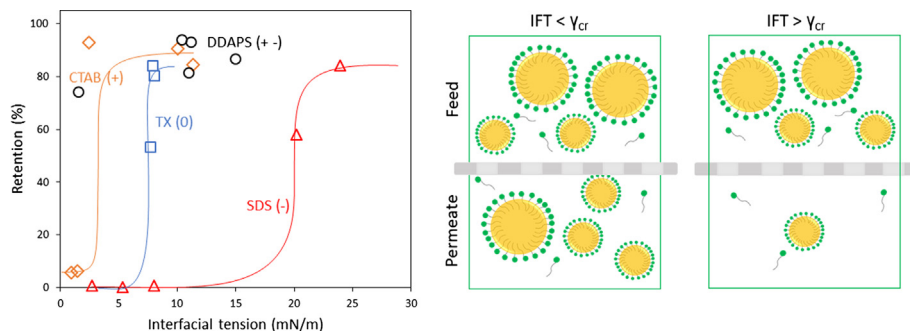
Surfactant-dependent critical interfacial tension in silicon carbide membranes for produced water treatment

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GRAPHICAL ABSTRACT



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ABSTRACT

During fossil oil extraction, a complex water stream known as produced water (PW), is co-extracted. Membrane treatment makes PW re-use possible, but fouling and oil permeation remain major challenges. In this work, membrane fouling and oil retention of Synthetic PW stabilized with a cationic, anionic, zwitterionic or nonionic surfactant, were studied at various surfactant and salt concentrations. We discuss our results in the framework of the Young-Laplace (YL) equation, which predicts for a given membrane, pressure and oil-membrane contact angle, a critical interfacial tension (IFT) below which oil permeation should occur. We observe such a transition from high to low oil retention with decreasing IFT for the anionic (SDS), cationic (CTAB) and non-ionic (TX) surfactant, but at significantly higher critical IFTs than predicted by YL. On the other side, for the zwitterionic DDAPS we do not observe a drop in oil retention, even at the lowest IFT. The discrepancy between our findings and the critical IFT predicted by YL can be explained by the difference between the measured contact angle and the effective contact angle at the wall of the membrane pores. This leads to a surfactant-dependent critical IFT. Additionally, our results point out that zwitterionic surfactants even at the lowest IFT did not present a critical IFT and exhibited low fouling and low oil permeation.

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1. Introduction

During the extraction of oil, for each volume of oil an average of three volumes of water are co-extracted [1]. This water is known as produced water (PW). It stems not only from natural well water, but also from water used to improve the extraction [2]. With the

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ongoing population growth and increased environmental stress, water treatment and re-use are becoming a necessity, especially in areas where water is already scarce.

PW is a very challenging water stream to treat due to its variable composition. Salinity, oil concentration, pH, dispersed solids and many other factors, may vary drastically from one location to another [3] and also change with well lifetime. Surfactants, added during oil and gas extraction to increase oil recovery from reservoirs, and to protect equipment (e.g. corrosion inhibitors), pose a further challenge to PW treatment. Surfactants stabilize the oil-water emulsion by creating smaller and more stable oil droplets (<10 μm), which makes separation by conventional methods, such as hydrocyclones and dissolved air flotation, much harder. These droplets can, however, be removed by membrane filtration [4].

Independent of the type, all membranes will eventually suffer from fouling [5]. This can be due to scaling, biofilm growth or in the case of oil-in-water emulsions, such as PW, the formation of an oil layer on top of the membrane surface and in its pores [6]. Fouling results in a decreased permeability, which in some cases may be hardly reversible. The type and extent of fouling depends on the water characteristics, membrane type and operational conditions. Because of their chemical and temperature resistance, ceramic membranes can be cleaned with much harsher chemicals and hot fluids, which can remove fouling without affecting the chemical stability of the membrane. In particular, SiC membranes are increasingly used in the treatment of oily waste waters [7–10]. The suitability of SiC as a membrane material is mainly based on its high water permeability, due to its high porosity and hydrophilicity.

When using membranes for filtration of oil-in-water emulsions, surfactant chemistry plays a crucial role in membrane fouling [11–13]. Surfactants not only stabilize oil droplets in water by absorbing at the oil-water interface, but subsequently they also determine the chemistry and charge of oil droplets. In a recent work, we investigated the effect of surfactant type and ionic strength on membrane fouling [14]. In particular, we found that the used surfactant is crucial in determining the extend and type of membrane fouling, especially at high ionic strengths. While fouling can be critical in determining the successful application of membrane filtration, it can be clear that also the permeation of oil is such a critical parameter. Unfortunately, clear understanding of oil permeation for the different surfactants and under different conditions is still missing. Surfactants not only change the chemistry and charge of the oil droplets but an added effect is to low the oil-water interfacial tension (IFT), which allows oil droplets to be more deformable and easier squeeze through the membrane pores. In this work, we use ionic strength, surfactant type and concentration to control and manipulate the IFT. This approach allows us to study the IFT influence on oil permeation through the pores of the membrane during the filtration of oil-in-water emulsions, such as PW. We compare and discuss our results in the framework of the Young-Laplace equation, which predicts, for a given pressure and membrane, a critical IFT below which oil permeation occurs.

1.1. Theory

In membrane fouling by oil-in-water emulsions, the interactions that take place at the oil-water-membrane interface(s) play a crucial role. Due to these interactions, the oil can adhere to the membrane surface, determining different degrees of fouling. Hydrophilic surfaces are less prone to fouling by organic compounds because the hydrophilic surface is covered by a thin layer of water molecules loosely bound by hydrogen bonding [12]. A good indication of the hydrophilicity of a membrane is given by

the contact angle θ between the water phase and the membrane surface. This is described by Young's equation,

$$\gamma_{om} = \gamma_{wm} + \gamma_{ow} \cos \theta, \quad (1)$$

where γ_{om} (mN/m) is the oil-membrane interfacial tension, γ_{wm} (mN/m) the water-membrane interfacial tension and γ_{ow} (mN/m) the oil-water interfacial tension. Young's equation is, however, based on the assumption that the surface is smooth, clean and that no chemical reactions take place.

In the case of oil-in-water emulsions stabilized with surfactants, the amount of surfactants adsorbed at the oil-water interface affects the IFT. A measure of the amount of moles surfactant per droplet surface area is given by the surface excess Γ (mol/m²), described as

$$\Gamma = -\frac{1}{RT} \frac{\partial \gamma_{ow}}{\partial \ln C}, \quad (2)$$

where R is the ideal gas constant, T the absolute temperature, C (mol/m³) the surfactant concentration. This equation comes from the Gibbs adsorption isotherm and Γ is roughly equal to the areal concentration of the surfactants at the oil-water interface. However, this is true for relatively high surfactant concentrations in the bulk.

From Eq. (2), we can see that an increase in surfactant concentration leads to lower IFT, and thus an increase in oil droplet deformability. This is very relevant to the case of an oil droplet permeating through a membrane pore. Effectively, oil droplets require less energy to change their shape and to squeeze through pores smaller than the droplet size. The pressure at which the droplets go into and through the pores is the so-called critical entry pressure (P_{cr} , bar) [15]. It can be calculated with the Young-Laplace (YL) equation,

$$P_{cr} = -\frac{\gamma_{ow} c_p \cos \theta}{A_p}, \quad (3)$$

with c_p (m) being the circumference of the pore, A_p (m²) the surface area of the pore and θ ($^\circ$) the contact angle of the oil droplet with the membrane. The presence of surfactants can affect the contact angle, since surfactants may adsorb at the membrane-liquid interface and change the oil-membrane interaction. Eq. (3) is valid for a liquid layer, i.e. for a oil droplet-membrane interface where the size of the membrane pore is very small compared with the droplet size. Since the ratio of the droplet and membrane pore size is in our case very large (>10), no correction is needed for Eq. (3) [16].

We performed all experiments at constant transmembrane pressure ($\Delta P = 0.1$ bar). Therefore, we can rewrite Eq. (3) and we can calculate a critical interfacial tension γ_{cr} for our membrane, as a function of the contact angle θ between the oil droplet and the membrane in water

$$\gamma_{cr} = -\frac{A_p \Delta P}{c_p \cos \theta}. \quad (4)$$

If the interfacial tension is the dominant parameter influencing oil retention, we expect oil permeation at or below γ_{cr} .

2. Experimental Section

2.1. Materials

For the preparation of synthetic PWs, we used DI water, sodium dodecyl sulfate (SDS, anionic, Sigma Aldrich, ACS reagent, 99.0%), hexadecyltrimethylammonium bromide (CTAB, cationic, Sigma Aldrich, for molecular biology, 99%), TritonTMX-100 (TX, nonionic, Sigma Aldrich, laboratory grade), N-dodecyl-N,N-dimethyl-3-aminio-1-propanesulfonate (DDAPS, zwitterionic, 97.0% (dried material, CHN)), n-hexadecane (Merck Schuchardt 99.0%) as the oil, Coumarin 6/ Neeliglow Yellow 196 (Neelikon) as fluorescent dye, and sodium chloride (NaCl, VWR, 100%). The membrane is a

CoMem© asymmetric silicon carbide (SiC) membrane of which characteristics are given in Table 1. All chemicals were used without further purification steps.

2.2. Emulsion preparation and characterization

We prepared artificial produced water emulsions following the protocol of our previous work [14]. PW is an oil-in-water emulsion, where the oily phase is dispersed in the aqueous phase, stabilized by corrosion inhibitors, biocides and extraction enhancers, which act as surfactants [12]. For this reason, we made each synthetic produced water by dispersing oil droplets of n-hexadecane in water using surfactants as stabilizers.

Since PW is a complex stream, it can be difficult to mimic. Usually anionic surfactants (such as SDS) or blends of different surfactants are used in enhanced oil recovery (EOR) to achieve a low IFT and therefore improve the extraction of oil from the well [17]. But surfactants are present in PW also as corrosion inhibitors and biocides and even as natural surfactants. This complex mixture of surfactants would not allow a more fundamental study of PW as proposed in this work. For this reason, rather than using mixtures of surfactants, in our work we make artificial PW with a single surfactant. While the zwitterionic surfactant (DDAPS) that we use in our study was less explored, all the other surfactants selected (SDS, CTAB and TX) are commonly employed as model surfactants to mimic PW [17–19].

To detect the amount of oil that permeates through the membrane, we added a fluorescent dye to n-hexadecane. As fluorescent dyes bleach over time, we prepared the colored oil freshly before each experiment. We first put approximately 5 mg of the dye powder in a test tube together with 8 mL of n-hexadecane, later we placed the tube in an ultrasonic bath for 10 min. Afterwards, we filtered the oil with a Millipore 0.45 μm filter to remove any remaining solid particles.

To ensure all emulsions have the same characteristics, we prepared a stock emulsion, which we then further diluted to obtain the desired salt (1, 10 or 100 mM) and surfactant concentration. The surfactant concentrations were all chosen to be 0.1, 0.2 and 1 times the critical micelle concentration (CMC) value in absence of salt. We prepared the stock emulsions by dissolving a surfactant (239.1, 478.2 or 2391 mg/L SDS; 34.6, 69.2 or 346 mg/L CTAB; 14.4, 28.8 or 144 mg/L TX; 100.6, 201.2 or 1006 mg/L DDAPS) in 1 L of DI water in a Duran® bottle (Duran 21801545) by mixing with a dispersing mixer (IKA® T25 digital Ultra-Turrax with S25N 18G element) for 4 min at 14,000 rpm. Then, we injected 2 g of colored oil near the mixer head and mixed for 10 min at 14,000 rpm. For the filtration experiment, we diluted the prepared 1 L of emulsion with DI water in a 20 L tank in order to end up with a 100 ppm n-hexadecane solution and the desired surfactant and NaCl concentration. This method is proven to make emulsions with a mean droplet size of 5 μm and distributed between 1 and 9 μm [14]. In this work no zeta potentials were obtained of the emulsions. For similar surfactant concentrations and ionic strength, oil-in-water emulsions are known to be strongly negatively charged for SDS (zeta potentials of –110 to –120 mV [20,21]), strongly posi-

tively charged for CTAB ($\sim +85$ mV [21,22]), slightly negative for TX (from –20 to –5 mV [23]) and negatively charged for DDAPS (from –35 to –45 mV [24]). SiC membranes are known to be strongly negatively charged (zeta potentials of –20 to –35 mV [11,25]) at neutral pH, at which all experiments were performed.

2.3. Membrane filtration

Filtration experiments were performed by using an OSMO-inspector cross flow membrane filtration system supplied by Convergence. The feed, permeate and concentrate flows are measured by Bronckhorst M15 mass flow meters. The emulsion is continuously stirred to minimize any creaming which was aided by recycling of the concentrate and permeate back into the 20 L feed bottle. Before each experiment the clean water flux was measured. The cleaning of the ceramic membrane is done with acid and base and extensive DI water flushing. Each experiment is performed at least twice and all data points are reported. A membrane filtration experiment consisted of filtering for 3 h at a ΔP of 0.1 bar and a flow rate of 60 kg/h, which corresponds to a crossflow velocity (CFV) of 7.6 cm/s ($\text{Re} \sim 230$). The SiC membranes that we used have a really high permeate flux/bar (3000 LMH/bar) and for this reason a relatively low pressure, such as 0.1 bar, already provides a high flux. The flux is the most relevant factor in fouling as it determines the transport of foulants towards the membrane surface. The permeability was constantly monitored. The low CFV (7.6 cm/s) was chosen to stimulate fouling, allowing for efficient fouling experiments. In a real PW treatment process, one would choose a higher CFV to allow shear to reduce and slow down membrane fouling.

2.4. Permeate analysis

We measured the oil retention by using a fluorescent dye method already reported in previous works [6,14]. The oil retention R (%) is defined as

$$R = 1 - \frac{C_p}{C_f} \quad (5)$$

where C_p and C_f are the oil concentrations (ppm) in the permeate and the feed respectively. Therefore, we took a feed and permeate sample at the same time and used those for analysis. We used the feed with fluorescent oil to make a calibration line. Subsequently we measured the fluorescence of the permeate on the same sample plate and determine the oil concentration in the permeate using the calibration line. We measured the fluorescence of the samples in a Perkin Elmer Victor3 Multilabel Plate Reader, using a protocol for Fluorescein (465 nm/510 nm, 1.0 s). The dilutions for the calibration line and permeate were injected in threefold in a 96-hole well plate. The volume of liquid in one hole was 200 μL . We took a permeate sample every 30 min during a filtration experiment.

2.5. Cleanability

The ability to clean membranes, called cleanability (CA), is given by:

$$CA = \frac{J_{AC}}{J_0} \quad (6)$$

where J_{AC} (LMH/bar) is the permeability after cleaning and J_0 the permeability of a completely clean membrane. Since pressure can slightly change during the experiments the fluxes are corrected with the actual trans membrane pressure, giving the membrane permeability (LMH/bar).

We determined two different cleanabilities. The first one, water cleanability, is based on the water flux after 15 min forward flushing ($\Delta P = 0.5$ bar), 15 min backwashing and 15 min forward flushing ($\Delta P = 0.5$ bar), all with DI water. The second one, chemical

Table 1
CoMem© asymmetric silicon carbide (SiC) ultrafiltration membrane characteristics.
*Pore size analysis reported in SI.

Carrier material	Silicon carbide (SiC)
Selective membrane material	Silicon carbide (SiC)
Channels	31
Single channel diameter	3 mm
Membrane area	0.09 m ²
Nominal pore size	150 nm*
Typical flux at 25 °C at 1 bar (non-fouled)	3000 Lm ⁻² h ⁻¹

cleanability, is instead based on the flux after the procedure that follows. The membrane was first flushed for 30 min with a 15 g/L NaOH solution at 85 °C and $\Delta P = 0.5$ bar, then for 30 min with DI water at room temperature and $\Delta P = 0.5$ bar, later backwashed for 30 min with DI water at room temperature, and finally flushed again for 30 min with DI water at room temperature and $\Delta P = 0.5$ bar. This procedure was then repeated but starting with a 15 min membrane flush with a 10 mL/L HNO₃ solution at 50 °C and $\Delta P = 0.5$ bar, instead of NaOH solution flush.

Before starting a new experiment, we made sure the water permeability was the same as the clean membrane water permeability (CWP). If the flux, after the cleaning procedures reported above, differed from the CWP, the membrane module was opened and the membrane cleaned with abundant water, pressurized air and ethanol, until the initial CWP was recovered.

2.6. Contact angle and interfacial tension measurements

Both types of measurements were performed on a contact angle and contour analysis instrument (Dataphysics OCA 35). The contact angle measurements were performed in captive bubble mode, where a droplet of colored hexadecane is captured under a SiC membrane slice in the aqueous solution with the desired surfactant concentration and salt. The interfacial tension measurements were instead performed with the pendant droplet technique, where a droplet of solution, made of water, salt and surfactant, was suspended in n-hexadecane from a stainless steel needle of 1.65 mm in diameter, which directly acted as a scale bar for the calculations. Image analysis of the droplet shapes for both contact angle and interfacial tension were performed with the apparatus software, which makes use of Young-Laplace fitting. For each type of synthetic PW the measurement was taken at least 5 times.

3. Results and discussion

In this section, we first discuss the effect of surfactant concentration and ionic strength on the IFT and oil-membrane contact angle. Subsequently, we discuss membrane performance regarding flux decline over time and oil retention per surfactant type. We finally discuss our results in the framework of the YL equation, where interfacial tension and contact angle can be used to predict the degree of oil-permeation.

3.1. Interfacial tension

As discussed in the theory section, the interfacial tension is seen as a key parameter in oil permeation, since it affects the deformability of oil droplets, and thus their potential to squeeze through membrane pores. Different kinds of synthetic PW were prepared in order to study the effect of surfactant type, surfactant concentration and ionic strength. All these parameters influence the interfacial tension at the hexadecane-water interface, albeit not to the same extend for all surfactants. The NaCl concentrations used are 1, 10 and 100 mM, while the surfactant concentrations used are 0.1, 0.2 and 1 times CMC. In Fig. 1A we show the effect of surfactant concentration on the interfacial tension, while in Fig. 1B we show the effect of ionic strength.

From Fig. 1A, we can clearly see that the IFT for SDS is higher than CTAB and DDAPS, whose IFTs are instead quite similar. Therefore, CTAB and DDAPS allow for more deformable oil droplets. From Fig. 1A it is possible to calculate the slope $(\frac{\partial \gamma}{\partial \ln C})$, which is normally used to calculate the surface excess Γ , as described by Eq. (2). The surface excess Γ is defined as the concentration of surfactant molecules at the interface plane, relative to that at a similar plane in the bulk [26]. For the three surfactants, for which the sur-

factant concentration was changed, namely CTAB, SDS and DDAPS, we calculated this slope, i.e. the effect of surfactant concentration on IFT. The surface excess Γ was estimated to be 1.9 $\mu\text{mol}\cdot\text{m}^{-2}$, 2.8 $\mu\text{mol}\cdot\text{m}^{-2}$ and 2.3 $\mu\text{mol}\cdot\text{m}^{-2}$, respectively for CTAB, SDS and DDAPS at CMC.

Next to the effect of surfactant concentration, there is the effect of ionic strength. CTAB has a positive hydrophilic head group while SDS has a negative one. DDAPS has a zwitterionic head group with no net charge, while TX has a nonionic headgroup. As a consequence, the only surfactants for which the IFT is visibly affected by ionic strength are the ones with a net charge, i.e. SDS and CTAB. The lowering of the interfacial tension with ionic strength in this salt concentration range was already reported in previous studies and it is due to the effect of charge screening, reducing the repulsion between the hydrophilic heads of SDS or CTAB increasing the amount of surfactant molecules adsorbed at the oil-water interface [14,27–29].

3.2. Contact angle

The contact angle was obtained from a droplet of colored hexadecane trapped under a SiC membrane in a cuvette filled with the aqueous phase, at the desired surfactant concentration and ionic strength. Contact angle plays a crucial role in oil permeation. A lower value of oil-membrane contact angle translates into lower required pressure to push the oil droplet through the membrane, see YL (Eq. (3)). The results of contact angle measurements are shown in Fig. 2. For all surfactants and ionic strengths, there is a rather high contact angle ($>130^\circ$), here indicating a rather hydrophilic surface and thus little spreading of the hydrophobic oil droplet. This suggests that rather low IFTs are required for oil to squeeze through the membrane pores. However, the contact angle we measured proves only the colloidal interactions that occur at the outer surface of the membranes. However, since the surface chemistry of the SiC membrane outer surface is the same as that of its pores we do not expect a big discrepancy between macroscopic contact angle and pore interior contact angle. For CTAB we see a slightly decreasing contact angle at increasing surfactant concentration (from $144^\circ \pm 6$ to $136^\circ \pm 5$) and a slightly increasing contact angle at increasing ionic strength (from $142^\circ \pm 3$ to $156^\circ \pm 5$). For SDS, the contact angles slightly increase with increasing surfactant concentration (from $157^\circ \pm 4$ to $173^\circ \pm 7$), while it slightly decrease at high ionic strength (from $173^\circ \pm 7$ to $159^\circ \pm 3$). For TX, we do observe little influence on the contact angle at increasing ionic strength. The contact angle is $150^\circ \pm 9$ at 1 mM, $172^\circ \pm 8$ at 10 mM and $172^\circ \pm 7$ at 100 mM. This is confirmed by a previous study, where wettability of charged surfaces was found to increase with ionic strength [30]. However, here the change is little. For DDAPS at 0.1 CMC contact angle was lower than for all the other surfactants ($106^\circ \pm 23$). With increasing surfactant concentration the contact angle reached similar values to the other surfactants. No clear effect of ionic strength was observed for DDAPS. Overall, the surfactants seem to have little effect on contact angle, and in all cases it remains rather high. This suggests that rather low IFTs are required for oil to permeate the membrane.

3.3. CTAB stabilized emulsions

In Fig. 3, we show the results of fouling studies with emulsions stabilized by the positively charged CTAB. In Fig. 3A and Fig. 3B, normalized flux decline curves, and average oil retentions, are displayed as a function of the surfactant concentration and ionic strength, respectively. The respective oil retentions as a function of permeate volume are shown in the Supplementary Information (SI, Figure S5).

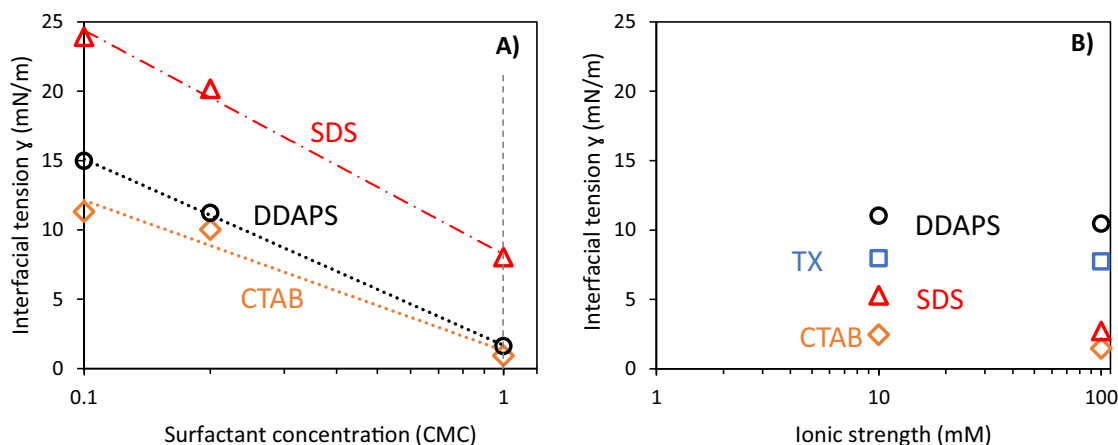


Fig. 1. Interfacial tension as a function of surfactant concentration (A) at 1 mM NaCl and ionic strength (B) for CTAB (69.2 mg/L, 0.2 CMC), SDS (2391 mg/L, CMC), DDAPS (201.2 mg/L, 0.2 CMC) and TX (144 mg/L, CMC). With CMC (2391 mg/L for SDS, 346 mg/L for CTAB, 144 mg/L for TX and 1006 mg/L for DDAPS) we indicate the surfactant critical micelle concentration in absence of salt. Symbols represent data points, while lines are based on Eq. (2). Error bars were smaller than the markers (standard deviation (SD) ≤ 0.6 mN/m, and are for that reason not shown). All the experiments were performed 5 times.

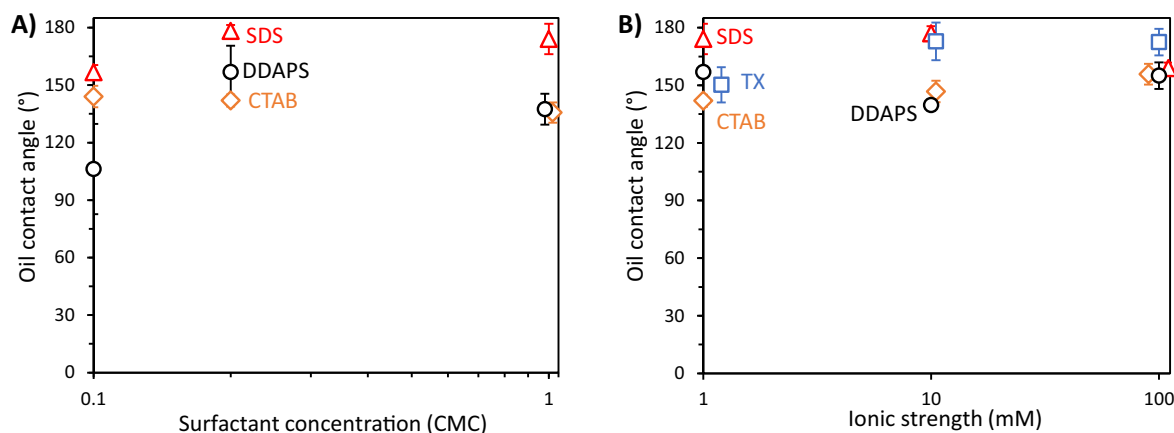


Fig. 2. Contact angle of oil on a slice of SiC membrane in water solution as a function of surfactant concentration (A) at 1 mM NaCl and ionic strength (B) for CTAB (69.2 mg/L, 0.2 CMC), SDS (2391 mg/L, CMC), DDAPS (201.2 mg/L, 0.2 CMC) and TX (144 mg/L, CMC). With CMC (2391 mg/L for SDS, 346 mg/L for CTAB, 144 mg/L for TX and 1006 mg/L for DDAPS) we indicate the surfactant critical micelle concentration in absence of salt. All the experiments were performed 5 times.

CTAB shows a high flux decline for all three surfactant concentration and ionic strengths, as shown in Fig. 3A and Fig. 3B. We can explain this behavior by looking at the electrostatic attraction between the negatively charged membrane, based on SiC [11], and the positively charged oil droplets (zeta potential of SiC membrane and CTAB emulsions described in Experimental Section (2.2)). This allows severe fouling to build up with limited influence of surfactant concentration and ionic strength. The flux decline is expected to stem from pore blocking, since we do not observe a strong influence of surfactant concentration and ionic strength that would be the main actors of a change in the cake layer resistance [14].

For the oil permeation however, we do see a very strong effect of concentration and ionic strength. At the lower surfactant concentrations we observe a stable high oil retention, but this drops to nearly 15% at the CMC. The same is observed for the ionic strength, high and stable retentions at 1 and 10 mM NaCl, but very low retentions at 100 mM. This sharp transition between high and low oil retention is very much in line with the predictions of YL equation (Eq. (5)), where oil permeation can occur below a critical interfacial tension. Both increasing the ionic strength, and increasing the surfactant concentration leads to a lower IFT (see Fig. 2). As shown in SI (Figure S5B and S5D), the PWs with the lowest inter-

facial tensions, 0.2 CMC at 100 mM NaCl and CMC at 1 mM show almost no oil retention (from 0 to ~10%) during filtration. This maybe caused by their low interfacial tensions, respectively 1.47 and 0.94 mN/m. This will be discussed in more detail in Section 3.7.

3.4. SDS stabilized emulsions

In Fig. 4, we show the results for the emulsions stabilized with negatively charged SDS.

For SDS both the effect of the electrostatic interactions and the interfacial tension are clearly visible in Fig. 4A. First of all, the decrease in oil retention follows the trend of the decrease in interfacial tension, as suggested by the YL equation. This even leads to nearly 0 retention at the CMC. Increasing SDS concentration from 0.1 and 0.2 to 1 time CMC, flux decline becomes less severe, probably due to the high oil permeation. Oil rather than accumulating at the membrane surface and in its pores, goes through the membrane, leading to less fouling. Furthermore, for this type of surfactant, the oil does not strongly adhere to the membrane surface, thus it does not cause a big flux decline and pore blocking, as observed for CTAB even at CMC. While for CTAB we observe a severe flux decline at CMC it does not occur for SDS stabilized emulsions at CMC. This effect may be related to the surface chemistry

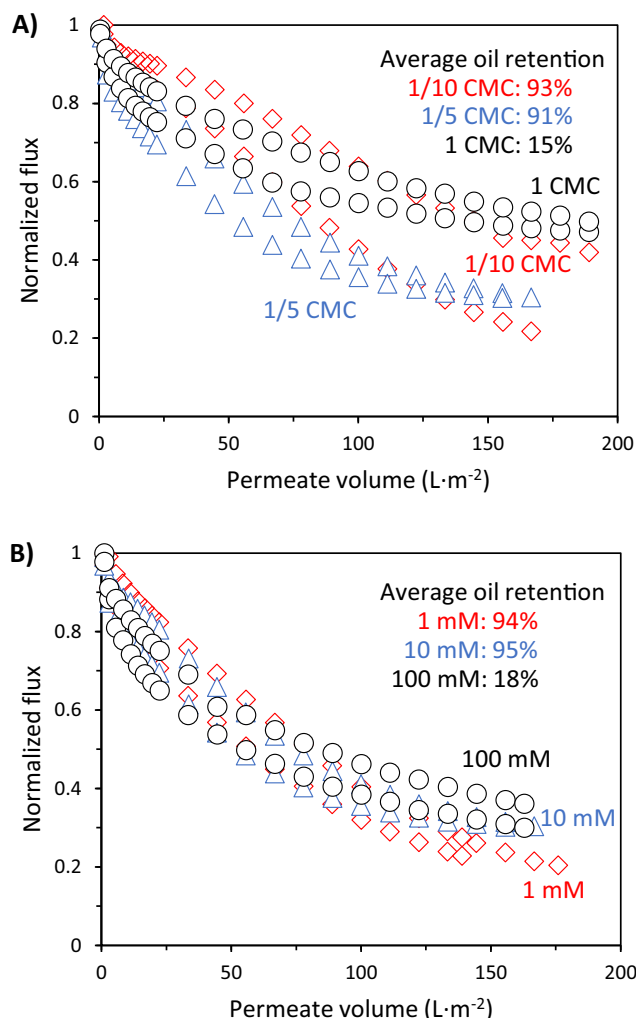


Fig. 3. Flux decline of CTAB stabilized emulsions and average oil retention at a crossflow velocity of 7.6 cm/s and a transmembrane pressure of 0.1 bar. Flux decline and average oil retention (A) as a function of surfactant concentration at 1 mM NaCl and (B) ionic strength at 0.2 CMC (69.2 mg/L CTAB). CMC = 346 mg/L is the critical micelle concentration for CTAB in absence of salt. All the experiments were performed in duplicate, as shown.

and charge of the surfactant. Since both membrane (SiC) and SDS are negatively charged (see SiC membrane and SDS emulsions zeta potential in Experimental Section (2.2)), the electrostatic interactions that take place at the oil-membrane interface are expected to reduce the oil adhesion.

In Fig. 4B we show the effect of ionic strength over fouling and average oil retention. In particular, we can see that there is not almost oil retention at all ionic strengths. The experiments are performed at CMC (value in absence of salt) and supposedly, below the critical interfacial tension for SDS. The ionic strength however has only a small effect on the flux decline. This decrease in flux decline with increasing ionic strength can be caused by a decrease in interfacial tension, which we displayed in Fig. 1B. Indeed, at lower IFT we expect a lower degree of pore blocking, since it becomes easier at low IFTs to push the oil through the membrane. We expect the interfacial tensions to be dominant since the increased charge screening would suggest a denser cake layer, leading to an increase in flux decline, which is opposite to our results. Dickhout et al. showed the effect of increased ionic strength at lower SDS concentrations, roughly 0.2 CMC, and found an increase in cake layer density though [27]. In our case, the lower interfacial tension makes

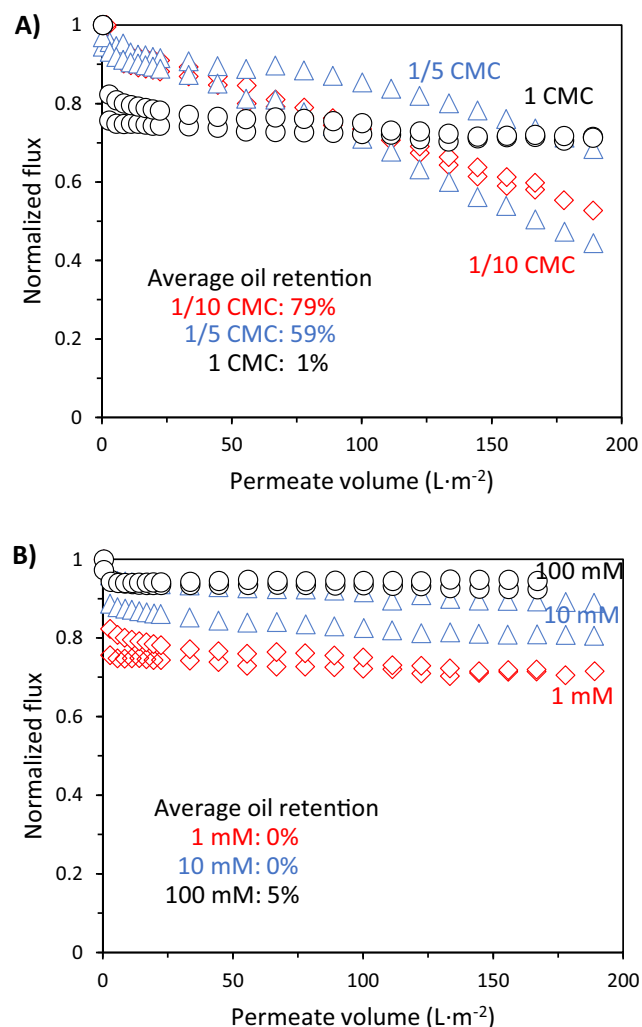


Fig. 4. Flux decline of SDS stabilized emulsions and average oil retention at a crossflow velocity of 7.6 cm/s and a transmembrane pressure of 0.1 bar. Flux decline and average oil retention (A) as a function of surfactant concentration at 1 mM NaCl and (B) ionic strength at CMC (2391 mg/L SDS). CMC = 2391 mg/L is the critical micelle concentration for SDS in absence of salt. All the experiments were performed in duplicate, as shown.

the oil droplets more deformable and thus easier to squeeze through the membrane, reducing the build up of oil at the membrane surface.

3.5. DDAPS stabilized emulsions

In Fig. 5, we show the results for emulsions stabilized by the zwitterionic DDAPS. The most striking result from Fig. 5A is the relatively low flux decline for all concentrations of DDAPS, compared to the flux declined of CTAB (Fig. 3A and B) and SDS (Fig. 4A). Furthermore, oil retention is relatively high. From Fig. 5B we can conclude that ionic strength has an effect on the flux decline, albeit not as clear as for the other ionic surfactants. Fig. 5C also suggests that there is an optimal ionic strength, 10 mM, at which flux decline is minimized. Oil retention, in contrast to flux decline, does not suffer from any ionic strength related effect and is above 85%, even at the highest ionic strength (100 mM). In contrast to SDS and CTAB, it seems that for DDAPS the critical interfacial tension has not been reached under these conditions.

The excellent hydration of sulfobetaines, such as DDAPS, was already investigated in other studies and showed that almost no

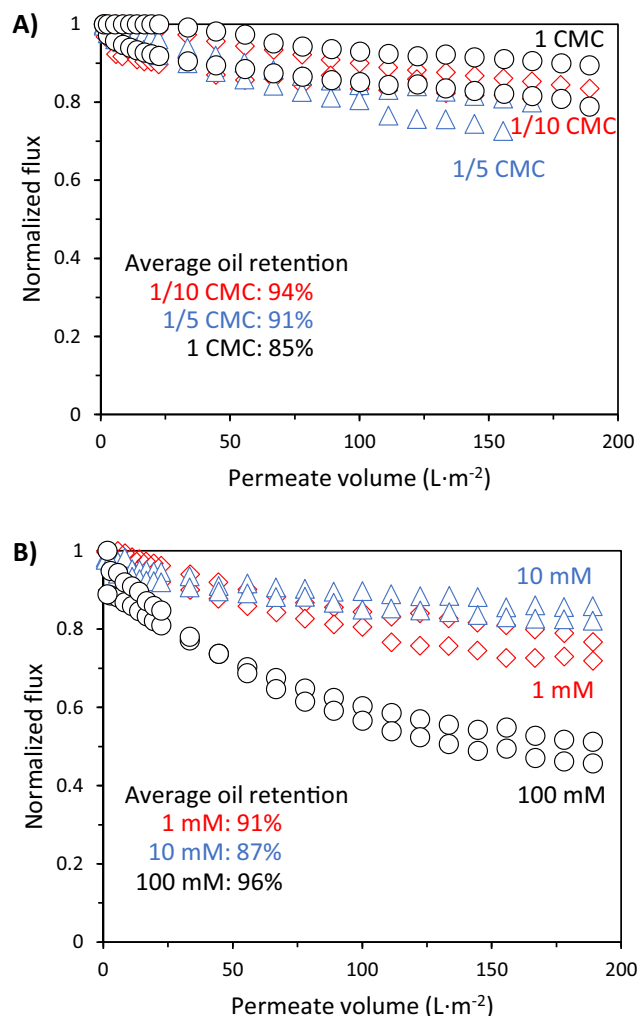


Fig. 5. Flux decline of DDAPS stabilized emulsions and average oil retention at a crossflow velocity of 7.6 cm/s and a transmembrane pressure of 0.1 bar. Flux decline and average oil retention (A) as a function of surfactant concentration at 1 mM NaCl and (B) ionic strength at 0.2 CMC (201.2 mg/L DDAPS). CMC = 1006 mg/L is the critical micelle concentration for DDAPS in absence of salt. All the experiments were performed in duplicate, as shown.

rearranging of water molecules was caused by dissolving these zwitterionic molecules [31–34]. Furthermore, for zwitterionic surfactants, in contrast with ionic surfactants, there is no counter ion release, which makes it energetically unfavorable for the DDAPS stabilized oil droplet to adsorb on the charged membrane surface [34]. DDAPS, thanks to its hydration properties, reduces the adhesion of the oil droplets at the membrane surface and even at higher ionic strengths avoids oil permeation. However, flux decline is more severe at 100 mM NaCl.

3.6. TX stabilized emulsions

In Fig. 6, we show the results for the nonionic TX. Here only the ionic strength experiments were performed.

The flux decline results are in close correspondence with those of Dickhout et al. [14]. Relatively high flux decline, is observed for all ionic strengths. The lack of electrostatic repulsion between the droplets and the membrane, but also between the droplets themselves, causes the rapid formation of a dense cake layer. If droplets adhere at the membrane surface the pore blocking also increases. Since the surfactant is not charged, no salt concentration effects were expected. Still, we do observe a clear effect of the ionic

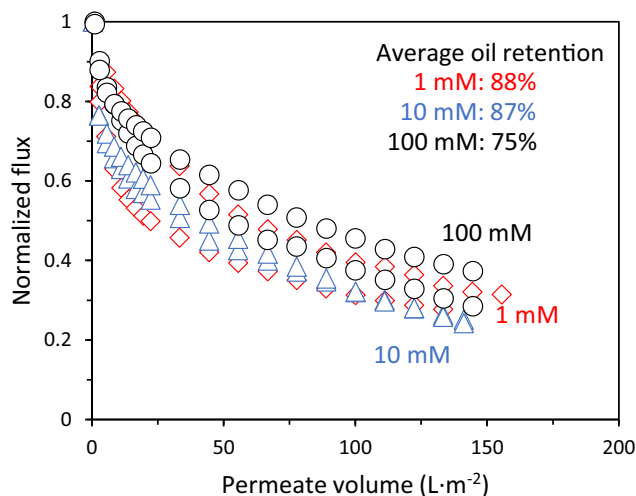


Fig. 6. Flux decline of TX stabilized emulsions and average oil retention at a crossflow velocity of 7.6 cm/s and a transmembrane pressure of 0.1 bar as a function of ionic strength at CMC (144 mg/L TX). CMC = 144 mg/L is the critical micelle concentration for TX in absence of salt. All the experiments were performed in duplicate, as shown.

strength on the oil retention. In addition, the membrane seems to behave differently at high ionic strength, showing an increased oil permeation with increasing permeate volumes (SI, Figure S8B). In Fig. 2 we did observe a small change in IFT for higher ionic strengths, even for the non-ionic TX. It could be that this small change is sufficient to get in IFT values below the critical one. This maybe a reason why here retention drastically changes over time.

3.7. Critical interfacial tension, surface chemistry and cleanability

In the previous sections, we discussed the effect of surfactant concentration and ionic strength for each type of surfactant. In Fig. 7, we show oil retention as a function of IFT for all data collected at different surfactant concentration and ionic strength.

We predicted the critical interfacial tension γ_{cr} by using Eq. (5), assuming contact angles of $130^\circ \leq \theta \leq 150^\circ$ (see Fig. 2) and we found a γ_{cr} of $0.37 \text{ mN/m} \leq \gamma_{cr} \leq 0.58 \text{ mN/m}$. Based on these calculations we predict a high oil retention for IFT values higher than

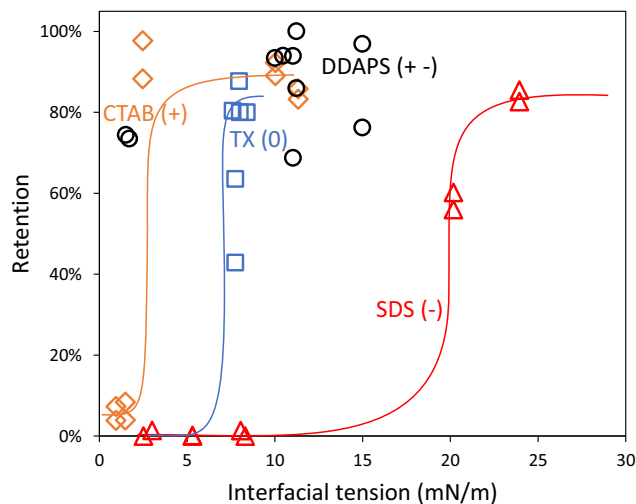


Fig. 7. Oil retention of CTAB, SDS, DDAPS and TX stabilized emulsions as a function of IFT at a crossflow velocity of 7.6 cm/s and a transmembrane pressure of 0.1 bar. All the experiments were performed in duplicate, as shown.

0.58 mN/m and low oil retentions below 0.37 mN/m. However, the predicted critical IFT γ_{cr} is very low and all the emulsions tested in this study have a higher IFT. Still, for CTAB, SDS and TX (see Fig. 7) we observed a clear transition from high to low oil retention with decreasing IFT. These experimentally observed critical IFTs are larger than the predicted one, with a critical IFT value specific to that surfactant. For CTAB, the oil retention drops for IFT values 3 times higher than the predicted critical value, while for SDS, the oil retention drops at IFT values almost 40 times higher than predicted. For the nonionic TX we observe a drop in oil retention from low to high ionic strengths at IFT~8 mN/m, value 15 times higher than predicted. On the other hand, the zwitterionic DDAPS was the only surfactant that did not show a critical IFT, even at the lowest IFT. If the IFT was the only responsible for oil permeation, we should expect no differences between oil retentions of different surfactant at similar IFT. Conversely, in Fig. 7 we do observe several data points with similar IFT but with highly different oil retention.

One would expect that the YL equation (Eq. (3)) would not lead to exact predictions for oil breakthrough, but such a big difference was unexpected. As shown in the Experimental Section, we performed contact angle measurements by injecting small droplets of oil under the exact same SiC membrane used in our filtration experiments. In addition, the contact angle measurements were performed in the presence of surfactant and salt, at exactly the same concentrations used in our filtration tests. Therefore, our experiments took into account adsorption of surfactants at the membrane-interface as well as surfactants adsorption at the oil-water interface. Still the very large discrepancy between our findings and the predicted critical IFT clearly indicates a substantial

difference between the measured macroscopic contact angle and the effective contact angle at the wall of the membrane pores [15,35,36]. This difference would also allow the surfactant-dependent critical IFT as observed by us.

In Fig. 8, we show membrane water cleanability and chemical cleanability, as defined in Section 2.5, as a function of surfactant concentration and ionic strength. For all the surfactants, the water cleanability slightly decreases by increasing surfactant concentration from 0.1 to 0.2 times CMC, while it increases from 0.2 to 1 times CMC (see Fig. 8A). SDS and DDAPS present a really good water cleanability, probably due to their surface chemistry (zeta potential of these emulsions are described in the Experimental Section (2.2)). SDS is negatively charged as the SiC membrane, while DDAPS has a zwitterionic chemistry, well known for its anti-fouling properties [31]. Conversely, CTAB is positively charged, and may strongly interact with the negative SiC membrane (see zeta potential of CTAB emulsions and SiC membrane in Experimental Section (2.2)), resulting in poor water cleanability even at the lowest surfactant concentrations. These results are confirmed by adsorption studies of surfactants on model silica surfaces, which have a comparable surface chemistry to SiC [6,37].

In Fig. 8B, we show the effect of ionic strength on water cleanability. SDS presents 100% flux recovery after cleaning with DI water, at all ionic strengths. For CTAB and TX we observe an increase in water cleanability as a function of ionic strength, while no clear trend is observed for DDAPS.

In Fig. 8C and D, we show the effect of chemical cleaning, with acid and base as described in Section 2.5, as a function of surfactant concentration and ionic strength, respectively. We can clearly see

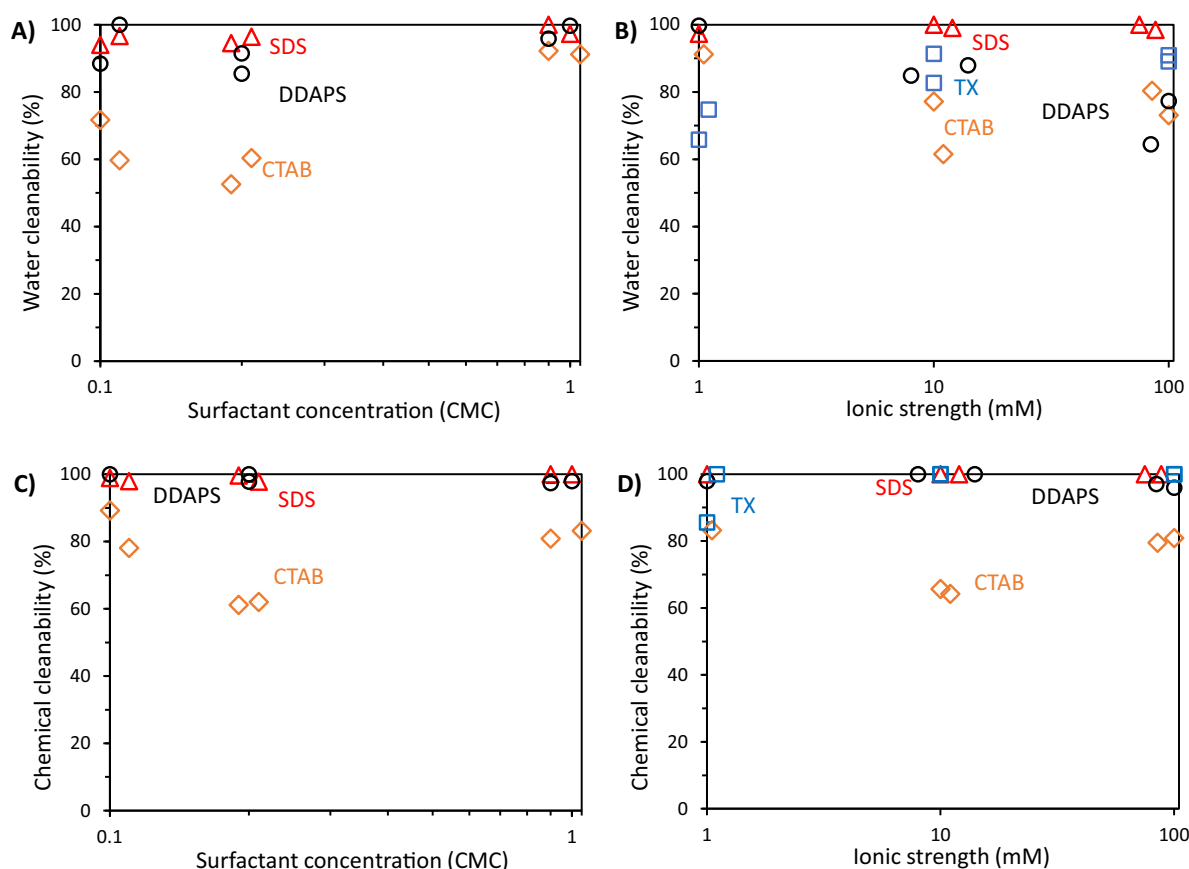


Fig. 8. Water cleanability and chemical cleanability of CTAB, SDS, DDAPS and TX stabilized emulsions as a function of surfactant concentration (A) (C) and ionic strength (B) (D). With CMC (2391 mg/L for SDS, 346 mg/L for CTAB, 144 mg/L for TX and 1006 mg/L for DDAPS) we indicate the surfactant critical micelle concentration in absence of salt. All the experiments are performed in duplicate, as shown.

that chemical cleaning helps in recovering almost 100% of the original flux for all the surfactants tested, with exception for CTAB. CTAB fouls the worst and this fouling seems difficult to remove.

The downside of the combination of a charged membrane and a charged surfactant is that ionic surfactants are influenced dramatically by ionic strength increases. This effect is shown by the poor oil retentions of CTAB and SDS at high ionic strength and at CMC, and it is also extensively described in literature [38], where it is shown that the added salt reduces interfacial tension and screens the electrostatic interactions. These effects become evident at the ionic strengths we adopted. Real PW can have even higher ionic strengths (up to 3000 mM [39]) and therefore fouling, and oil permeation, can be worse. Such high ionic strengths lead to several issues, such as fast coalescence of oil droplets and surfactant precipitation, also in real PW. For this reason, and in order to study oil permeation and fouling from a fundamental point of view, in this work we only focus on ionic strengths up to 100 mM. Nonionic surfactants like TX do not show the same dependency on ionic strength but at the same time lack of electrostatic repulsion all together, showing very high flux declines probably due to denser cake layers. Even though the ionic strength does not have the same influence on TX, as with charged surfactants, it is still capable to reduce the oil retention.

Out of the four surfactants used, our results show that DDAPS is the most promising. At the investigated experimental conditions, DDAPS shows excellent retention and maintains a high flux, although it is influenced by a ionic strength increase. This is proved by the increased flux decline at 100 mM NaCl, while switching from 1 to 10 mM we have a lower flux decline. DDAPS gives high flux and high oil retention even at low surfactant concentrations. From a membrane treatment perspective, these results imply that zwitterionic surfactants offer the best characteristics for surfactant based oil recovery.

4. Conclusions

In this work, by tuning ionic strength and surfactant concentration of our PW, we controlled the oil-water interfacial tension and investigated its influence on oil breakthrough for a SiC CoMem® membrane. For this, we used synthetic PW, consisting of n-hexadecane stabilized by cationic CTAB, anionic SDS, zwitterionic DDAPS or nonionic TX. Surfactant concentrations studied were 0.1, 0.2 and 1 times CMC, while ionic strengths were 1, 10 and 100 mM NaCl. We discuss our results in the framework of the Young-Laplace equation, which predicts for a given membrane and pressure, a critical interfacial tension γ_{cr} below which oil permeation should occur. We observe such a transition from high to low oil retention with decreasing IFT for the anionic, cationic and non-ionic surfactant, but with significantly higher critical IFTs than predicted. For the cationic CTAB, our membrane is performing less well, since oil retention drops for IFT values 3 times higher than the critical one. For the anionic SDS, the oil retention drops for IFT values almost 40 times higher than expected. For the nonionic TX we observe a relative drop in oil retention with increasing ionic strength for IFT values 15 times higher than predicted. On the other hand, the zwitterionic DDAPS was the only surfactant that did not show a critical IFT, even at the lowest IFT. We propose that our simple contact angle measurements do not take into account the complex interactions that occur at the wall of the membrane pores. These surfactants may play a crucial role, and as a consequence, at the pore wall we must expect a contact angle that is different from the one we measured. We can conclude that surfactants stabilized O/W emulsions have a critical IFT highly dependent on the type of surfactant used. Additionally, our results point out that zwitterionic surfactants, that even at the lowest IFT

did not present a critical IFT, are highly interesting for future studies and applications.

CRedit authorship contribution statement

Ettore Virga: Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing - original draft, Visualization, Supervision, Project administration. **Bernard Bos:** Validation, Investigation, Data curation, Visualization. **P.M. Biesheuvel:** Writing - review & editing, Visualization, Funding acquisition. **Arian Nijmeijer:** Writing - review & editing. **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.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcis.2020.03.032>.

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