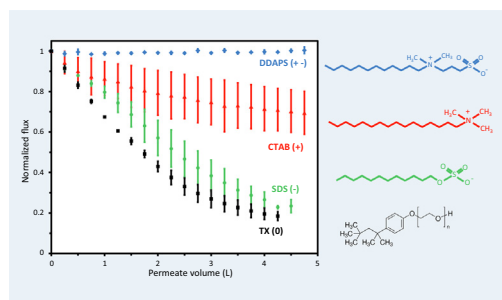


Regular Article

Surfactant specific ionic strength effects on membrane fouling during produced water treatment

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GRAPHICAL ABSTRACT



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ABSTRACT

Membrane filtration is a technique that can be successfully applied to remove oil from stable oil-in-water emulsions. This is especially interesting for the re-use of produced water (PW), a water stream stemming from the petrochemical industry, which contains dispersed oil, surface-active components and often has a high ionic strength. Due to the complexity of this emulsion, membrane fouling by produced water is more severe and less understood than membrane fouling by more simple oil-in-water emulsions. In this work, we study the relation between surfactant type and the effect of the ionic strength on membrane filtration of an artificial produced water emulsion. As surfactants, we use anionic sodium dodecyl sulphate (SDS), cationic hexadecyltrimethylammonium bromide (CTAB), nonionic TritonTMX-100 (TX) and zwitterionic N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS), at various ionic strengths (1, 10, 100 mM NaCl). Filtration experiments on a regenerated cellulose ultrafiltration (UF) membrane showed a pronounced effect of the ionic strength for the charged surfactants SDS and CTAB, although the nature of the effect was quite different. For anionic SDS, an increasing ionic strength leads to less droplet-droplet repulsion, allowing a denser cake layer to form, resulting in a much more pronounced flux decline. CTAB, on the other hand leads to a lower interfacial tension than observed for SDS, and thus more deformable oil droplets. At high ionic strength, increased surfactant adsorption leads to such a low oil-water surface tension that the oil droplets can permeate through the much smaller membrane pores. For the nonionic surfactant TX, no clear effect of the ionic strength was observed, but the flux decline is very high compared to the other surfactants. For the zwitterionic surfactant DDAPS, the flux decline was found to be very low and even decreased with increasing ionic strength, suggesting that membrane fouling decreases with increasing ionic strength. Especially promising is that at lower surfactant concentration (0.1 CMC) and high ionic strength no flux decline was observed, while a high oil retention (85%) was obtained.

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From our results, it becomes clear that the type of the surfactant used is crucial for a successful application of membrane filtration for PW treatment, especially at high ionic strengths. In addition, they point out that the application of zwitterionic surfactants can be highly beneficial for PW treatment with membranes.

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1. Introduction

Membrane filtration is an increasingly important technique for the treatment of a wide spectrum of waste waters from a large variety of sources [1–6]. Membranes are, for example, used for municipal waste water treatment in combination with bioreactors [7], and in the food industry both in the processes themselves [8,1] and as waste water treatment for factory effluents [9,10]. Moreover, membrane filtration is used to remove harmful chemicals and particles, such as heavy metals or oil and grease, from industrial waste streams. Treating these wastewaters sufficiently brings the water to such quality that it also allows its re-use, thereby decreasing the fresh water demand. This large variety of applications and feed streams means that membrane filtration has to be tailored to each specific process. The membrane material, process parameters and pretreatment, all influence the performance of the membrane system and therefore have to be carefully chosen. This is especially important, as virtually all membrane processes suffer from fouling, the building up of retained material on the feed side of the membrane [6]. In membrane fouling, the foulant adhesion/deposition is a thermodynamic mechanism based on energy balance principles [11] that can cause filtration resistances driven by chemical potential differences [12,13]. Fouling blocks the pores, builds into a cake layer and thereby reduces the membrane flux and increases operational costs. In some cases, however, this cake layer on top of the membrane forms a new active layer and improves the filtration characteristics of the membrane [14].

A current focus area of membrane science is the use of membranes to treat the challenging water stream of so-called produced water (PW), a very large water stream that stems from the petrochemical industry and has the potential to act as a substantial source of water for re-use. Quite some research has now shown that PW can be effectively treated using membrane filtration, but that membrane fouling remains a critical problem [15,6]. PW contains dissolved and dispersed hydrocarbons, salts, heavy metals and solid particles, as well as production chemicals. Before this water can be re-used or disposed, those components have to be removed. For example, to meet the OSPAR regulations dispersed oil in PW discharges should not exceed a concentration of 30 mg/L [16]. The dispersed oil can be removed largely by conventional techniques such as gas flotation, adsorption, evaporation and hydrocyclones, but the smallest oil droplets with a size <10 µm are less efficiently removed by these techniques [17]. Membrane filtration can remove those droplets, but, as mentioned, the fouling of the membrane by these oil droplets is often severe. Moreover, the membrane fouling by produced water is typically more severe than membrane fouling by many other oil-in-water emulsions such as food emulsions or other industrial waste waters containing oils [18]. One parameter that widely changes from source to source is salinity [6], highly affected by the geochemistry of the reservoir [19]. Therefore, ionic strength is an important parameter to investigate. A high salinity can have a detrimental effect of the stability of the stabilized oil droplets, which in turn can lead to more detrimental fouling [20]. It is good to mention that produced water is a stream with varying properties. The composition of produced water changes from well to well but also over the lifetime of an oil reservoir [21]. Therefore, there

is no universally applicable solution or method for all sources of produced water.

In order to control membrane fouling by produced water, it is important to understand the interaction of the oil droplets with the membrane surface. Here the presence of surfactants is believed to play a key role. The surfactant adsorbs to the oil-water interface of the droplets, but also often adsorbs to the membrane surface. The surfactant will thus determine much of the interactions between droplet and membrane surface, and naturally the droplet-droplet interactions. Since PW contains such a variety in components, it is important to understand what the influence of each component is on the membrane fouling, but also how one component might affect the fouling propensity of another component. For example, the effective stabilization of an oil droplet by a charged surfactant will be strongly influenced by the ionic strength, while for an uncharged surfactant the ionic strength might play only a small role.

In literature, many examples of oil-water separation with membranes can be found, as well as studies on the kinetics of fouling. Here, we will discuss a few examples in which the influence of emulsion components or process parameters was studied systematically. Li et al. developed a cellulose ultrafiltration (UF) hollow fiber membrane for oil-water separation [22]. They chose cellulose for its high resistance against swelling from organic compounds and its hydrophilic nature. The retention was 99% for an emulsion of machine oil in water while showing only minimal fouling, showing the potential for this membrane material. Lipp et al. also tested a cellulose membrane for oil-in-water emulsion separation. Their emulsion contained a mixture of oil and surface-active components [23]. They found evidence of coalescence in the cake layer, and proposed a loss of surfactant to the permeate due to this coalescence, thereby changing the properties of the cake layer, making it more dense. Out of a range of membranes, however, the regenerated cellulose membrane showed excellent oil rejection and flux recovery after cleaning. Lu et al. studied the filtration of oil-in-water emulsions with three different surfactants on a ceramic membrane [24]. Interestingly enough, they found that an emulsion with surfactant oppositely charged to the membrane surface charge showed less irreversible fouling than a surfactant with similar charge. They attributed this effect to the adsorption of surfactant molecules to the surface and the inside of the membrane pores, hindering the entrance of oil into the membrane. The exact mechanism however was not understood well and requires further investigation. Singh et al. studied the influence of the ionic strength on membrane fouling during aqueous filtration of silica particles [25]. They found that the fouling potential of the feed water was linearly related to the double layer thickness. In their experiments and model, a 10-fold increase in ionic strength had the same effect as a 2-fold increase in colloid concentration of the feed.

What becomes apparent from the discussed studies, is that the effect of many parameters, such as type of surfactant, type of membrane surface, ionic strength etc., have received prior interest. However, all studies look at just a single parameter at the same time, while it is clear that a parameter such as surfactant type, could strongly influence the effect for the ionic strength. In this work, we chose four different model surfactants with different

properties. We used an anionic, cationic, nonionic and zwitterionic surfactant and compare their behavior when used in membrane filtration experiments. In addition, we varied the salt concentration of the feed emulsion to study the effect of ionic strength on membrane fouling, and how that is affected by the type of surfactant. The emulsions used in this study are synthetic model emulsions with carefully chosen components, so we are able to control the properties of the emulsions.

2. Theory

Here we provide the theoretical background that is the basis for all interpretation of the experimental data. After prolonged filtration of oily waste water, we expect that the membrane fouling will be dominated by a cake layer formed on the membrane surface [26,27]. Therefore we study the effect of increasing ionic strength on membrane fouling by oil-in-water emulsions stabilized by four different surfactants. Since the properties, and especially the charge of the head group of those surfactants are different, we expect to see an influence on the formed cake layer and thus the observed flux decline. Here we link the expected properties of the cake layer, described by the Kozeny-Carman term, to the DLVO theory. We also discuss the critical pressure required to push an oil droplet through a membrane pore.

The resistance of a cake layer on the membrane can be described by the Kozeny-Carman term

$$R_c = \frac{150l_c(1 - \varepsilon_c)^2}{D_v^2 \varepsilon_c^3}, \quad (1)$$

where l_c is the thickness of the cake layer, ε_c the porosity of the cake layer and D_v the effective diameter of the oil droplets [28]. This resistance is heavily dependent on the porosity ε_c of the cake layer, and therefore of the interaction between the droplets in the cake layer. As shown in previous work [29], the pores in a cake layer of monodisperse particles are not effective in rejecting oil droplets based on pore size, as the pores in the layer are larger than the membrane pores.

At fixed oil concentrations, droplet sizes, crossflow velocities and initial fluxes, the properties of the cake layer will to a large extent be governed by droplet-droplet interactions. The interaction between two colloidal particles, in our case oil droplets, can be described by the DLVO theory. This theory adds the attractive interaction energy V_A and the repulsive interaction energy V_R in the total potential V_T

$$V_T = V_A + V_R. \quad (2)$$

It is possible to extend the DLVO by including a hydration energy term [30]. However, since this goes beyond the scope of this manuscript, we refer to the classical DLVO theory. The attractive van der Waals potential, caused by the alignment of dipoles in adjacent molecules, can be found by calculating the interaction of one atom in a droplet with all the atoms in a second droplet, leading to a long-range interaction. When the particle separation distance h is small compared to the droplet radius a ($h \ll 2a$), the potential V_A , expressed in J, is given by

$$V_A = -\frac{Aa}{12h} \quad (3)$$

where A is the Hamaker constant, which depends on the polarizability of the droplet material. Thus, the attractive potential between two oil droplets is inversely dependent of the separation distance between the droplets. While the used surfactant will have some influence on the attractive van der Waals potential, it will be dominated by the droplets bulk material. The surfactant type and

the ionic strength will therefore have limited influence on the attractive interaction between droplets.

The electrostatic repulsion is an important stabilizing factor in oil-in-water emulsions. When the oil droplets carry a surface charge, the repulsion will prevent collision between the droplets. For short distances h , the electrostatic repulsion V_R , also expressed in J, can be written as

$$V_R = 2\pi\epsilon_0\epsilon_r a\psi_\delta^2 \exp(-\kappa h) \quad (4)$$

where ψ_δ is the surface potential of the oil droplet. This electrostatic repulsion is dependent on the thickness of the electrostatic double layer (EDL) or the Debye length ($1/\kappa$, expressed in m), which is given by

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2N_A e^2 I}} \quad (5)$$

where ϵ_0 is the permittivity of vacuum, ϵ_r the dielectric constant of the medium, k_B is the Boltzmann constant, T is the absolute temperature, N_A Avogadro's number, e the elementary charge and I the ionic strength of the emulsion.

The total interaction energy V_T , as stated in Eq. (2), results in a potential curve with a maximum which has to be overcome for droplets to come in close contact. As can be seen from Eqs. (4), (5), the repulsive force is dependent on the ionic strength of the emulsion. At increasing ionic strength, the repulsive forces between charged droplets decreases, allowing the droplets to come into much closer contact, or even to coalesce. At higher ionic strength more surfactant will adsorb to the droplet surfaces, thereby increasing the surface charge density. The screening effect of salt that lowers the electrostatic repulsion between droplets is, however, stronger than the increased repulsion due to the additional surfactant on the surface [31].

Droplets stabilized by nonionic surfactants however do not carry a surface charge. They stabilize the oil droplets by steric hindrance of a large hydrophilic head group [32]. As this interaction is not charge based, the ionic strength will have little effect on the strength of steric stabilization.

Zwitterionic surfactants stabilize by hydration of the head group. In contrast to charged surfactants, the water molecules around the head group are ordered in the same manner as in the bulk phase of water instead of reordering the water around the single charge of an ionic surfactant [33]. In this unperturbed state, the water molecules around the zwitterionic group are in a H-bonded structure, which takes a considerable amount of energy to disturb.

When a cake layer is formed on the membrane surface, we expect that the repulsive forces between oil droplets with charged surfactants contribute to the porosity of the cake layer. Because the surface charge of the droplets and the resulting electrostatic repulsion, we expect a more open cake layer and less flux decline. However, at increasing ionic strength, the electrostatic repulsion decreases and the cake layer is expected to become more dense because of electrostatic screening of the surface charge. For non-ionic and zwitterionic surfactants, which suffer less from electrostatic screening, we expect that increasing the ionic strength has a less pronounced effect on the flux decline. For these surfactants especially the steric repulsion and head group hydration will dominate. It is important to mention that for zwitterionic surfactants, the hydration of the headgroup typically does depend on the ionic strength. At higher ionic strength, the headgroup will be more hydrated and a larger repulsion could follow. So for zwitterionic surfactants, a higher ionic strength might even lead to a more open cake layer and thus a lower flux decline [34].

Apart from the membrane flux, a key membrane performance parameter in PW treatment is the retention of oil droplets. While in this study the membrane pores are much smaller than the oil

droplets, oil droplets can deform to flow through the pore if the applied pressure is large enough. The critical pressure difference P_{crit} (in bar) at which oil transport through the membrane starts to occur can be estimated by:

$$P_{crit} = -\frac{\gamma O_p \cos \theta}{A_p} \quad (6)$$

where γ is the interfacial tension between the oil and the aqueous phase, O_p the circumference of the pore, θ the advancing contact angle of the droplet on the surface and A_p the surface area of the membrane pore. As can be seen, a key parameter here is the oil-water interfacial tension. For charged surfactants the interfacial tension is a function of the ionic strength. The higher the ionic strength, the lower the repulsion between headgroups, allowing more surfactant molecules to adsorb at the oil-water interface. Ideally, the contact angle used to calculate the critical pressure should be measured on a smooth polymer film, to exclude any effects of roughness. Here we used the contact angle on a rougher surface (the membrane) as in the previous works no significant difference in contact angle was observed between the cellulose membrane and a spincoated cellulose film [35]. The adsorbed amount of surfactant at the oil droplet surface Γ_s (expressed in mol/m²), at constant temperature T and pressure p , can be derived from the interfacial tension γ via

$$\Gamma_s = -\frac{C}{RT} \left(\frac{\delta \gamma}{\delta C} \right)_{T,p} \quad (7)$$

where R is the ideal gas constant, and C is the surfactant concentration. For charged surfactants, a higher ionic strength leads to a lower interfacial tension, and as a consequence it lowers the critical pressure at which the oil droplets can be pushed through the membrane. For non-ionic and zwitterionic surfactants this effect is not expected.

3. Materials and methods

3.1. Materials

For preparation of the emulsions, we used DI water, sodium dodecyl sulfate (SDS, Sigma Aldrich, ACS reagent, 99.0%), hexadecyltrimethylammonium bromide (CTAB, Sigma Aldrich, for molecular biology, 99%), Triton™X-100 (TX, Sigma Aldrich, laboratory grade), N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS, 97.0% (dried material, CHN)), n-hexadecane (Merck Schuchardt 99.0%) as the oil, Coumarin 6/ Neelglow Yellow 196 (Neelikon) as fluorescent dye, and sodium chloride (NaCl, VWR, 100%). The membrane used was a regenerated cellulose UF membrane with a pore size of 500 kDa (Microdyn Nadir UC500T). All chemicals were used without further purification steps.

3.2. Emulsion preparation and characterization

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

To ensure all emulsions have the same characteristics, a stock emulsion was prepared, which was then further diluted to obtain the desired salt and surfactant concentration. The surfactant concentrations were all chosen to be at or below the CMC, but high enough to ensure a stable emulsion and a reproducible droplet size distribution. The stock emulsions were prepared by dissolving a

surfactant (463 mg/L SDS; 346 mg/L CTAB; 298 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 2 min at 14,000 rpm. Then, 2 g of colored oil was injected near the mixer head and mixed for 10 min at 14,000 rpm. The stock emulsion was diluted to contain 100 mg/L hexadecane and the desired surfactant and NaCl concentration to make up 20L of feed emulsion. The particle size distribution was determined with a DIPA 2000 - Particle Analyzer (Prolyse). The mean droplet size in the diluted emulsions was 4 µm, with a rather broad distribution in droplet sizes (± 3) and was constant for all conditions. 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 [36,37]), strongly positively charged for CTAB ($\sim +85$ mV [37,38]), slightly negative for TX (from -20 to -5 mV [39]) and negatively charged for DDAPS (from -35 to -45 mV [40]). Regenerated cellulose membranes are known to be negatively charged (zeta potentials of -8 to -25 mV [41–43]).

3.3. Membrane filtration

The membrane filtration experiments were performed using an OSMO-inspector crossflow membrane filtration system built by Con-Vergence. A fresh membrane sheet was used for each experiment. The membrane was mounted in a flat sheet crossflow membrane cell with an effective surface of 240 cm², using a feed spacer with a thickness of 700 µm, a filament angle of 90° and a maze size of 2.5 × 2.5 mm. The volume and density of the feed and permeate streams were measured by Bronckhorst M15 mass flow meters. The 20 L glass feed bottle was constantly stirred to prevent creaming of the feed. Both concentrate and permeate were recycled to the feed bottle to ensure a consistent feed quality. Before mounting the membrane, it was soaked in DI water overnight to remove production chemicals and glycerine from the membrane. Then, the clean water flux was measured. A membrane filtration experiment consisted of filtering for 3 h at a TMP of 1 bar and a flow rate of 48 kg/h, which corresponds to a crossflow velocity of 0.2 m/s. This crossflow velocity corresponds to laminar Reynolds ($Re \sim 220$) making it is possible to neglect droplets break up due to shear stress in our system [44]. The permeate flux was constantly monitored. To clean the membrane, the cell was flushed with DI water for 1 h without applied transmembrane pressure, then a backflush with DI water of 3 min at 0.2 bar, and then another flush. After the cleaning, the clean water flux was measured again to determine the flux recovery. Each experiment was repeated at least two times and an average and standard deviation were taken on the basis of these data.

3.4. Permeate analysis

The oil retention for SDS based emulsions was measured by liquid-liquid extraction of the permeate and subsequent HPLC analysis as described in previous work [29]. For the other surfactants, the fluorescent dye method was used, because the presence of surfactants often caused excessive foaming, hindering the extraction. We repeated the fluorescence method for SDS based emulsions and found good agreement with the results obtain by extraction.

The oil retention R (%) is defined as

$$R = \left(1 - \frac{F_p}{F_f} \right) \quad (8)$$

where F_p and F_f are the oil concentrations in the permeate and the feed respectively. Therefore, we took a concentrate and permeate

sample at the same time and used those for analysis. The concentrate with fluorescent oil was used to make a calibration line. The permeate was subsequently measured on the same sample plate to determine the oil concentration in the permeate using this calibration line. The fluorescence of the samples was measured 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 μ L. As shown in previous studies [29], the rejection of oil does not change significantly over the course of the experiment, therefore we took the permeate sample only once, after 2 h of filtration.

3.5. 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 n-hexadecane is captured under a piece of membrane in the aqueous solution with surfactant and salt. The interfacial tension measurements were performed with the pendant droplet technique [45,29], where a droplet of aqueous solution with surfactant and salt is suspended in colored n-hexadecane in a cuvette. Image analysis of the droplet shapes from both contact angle and interfacial tension measurements was performed with the software provided with the measuring instrument, taking into account the density of the media. These experiments were repeated at least two times, and average and standard deviations were obtained from these data.

4. Results

In this section, we will first discuss background data on the contact angle and interfacial tensions for four different surfactant types, at three different salt concentrations. Membrane performance data regarding flux decline over time, oil retention and flux recovery after cleaning are then discussed per surfactant type.

4.1. Interfacial tension

The interfacial tension was measured using the pendant droplet technique, where a droplet of aqueous solution is suspended in a cuvette filled with colored oil. The results are plotted in Fig. 1. It is immediately apparent that the four different surfactants show different behavior.

SDS, the anionic surfactant, provides the highest oil-water interfacial tension at low ionic strength. At 1 mM NaCl, the interfacial tension is 18.2 ± 5 mN/m, decreasing to 12.4 ± 0.5 mN/m for 10 mM NaCl and 2.3 ± 0.2 mN/m for 100 mM NaCl. This strong dependence on the ionic strength indicates that the adsorbed amount of surfactant depends on the ionic strength. Upon increasing the ionic strength, the charge of the head groups is screened, allowing more surfactant molecules to adsorb to the droplet surface, leading to a lower interfacial tension.

CTAB, the cationic surfactant, shows the lowest interfacial tensions of the four. CTAB has the longest carbon tail of all surfactants studied here, leading to a higher adsorbed amount and thus a lower interfacial tension. At 1 mM NaCl, the interfacial tension is 1.9 ± 0.3 mN/m, lowering to 0.4 ± 0.1 mN/m and 0.3 ± 0.1 mN/m for 10 and 100 mM respectively. These last two values are not accurate because the pendant droplet technique is not appropriate to study such low interfacial tensions. There is a clear decrease in interfacial tension between 1 and 10 mM however, so we can assume that we have a similar situation as with SDS, where the screening of charges at the head group of the surfactant molecules allows more

surfactant molecules to adsorb, leading to a lower interfacial tension at higher ionic strengths. Based on this data we cannot confirm that this trend continues from 10 mM to 100 mM of salt, but this would be expected.

As expected, for TX-100, the non-ionic surfactant, an increase in ionic strength does not influence the adsorption of surfactant to the droplet surface very much. The interfacial tensions for 1, 10 and 100 mM are 6.7 ± 0.6 mN/m, 8.0 ± 0.1 mN/m and 7.8 ± 0.1 mN/m respectively. The small variation in interfacial tension could be caused by small changes in the solvent quality for the polyethylene oxide tail of TX upon the addition of salt.

The interfacial tension of DDAPS stabilized droplets also does not change significantly with increasing salt concentration. The interfacial tension is 2.5 ± 0.1 mN/m, 2.4 ± 0.1 mN/m and 2.4 ± 0.1 mN/m for 1, 10 and 100 mM respectively. As was the case with CTAB, these values are in a regime that is hard to measure accurately using the pendant drop technique. The head groups of DDAPS are neutral as a whole, but do have a positive and a negative charge on their head groups [34].

4.2. Contact angle

The contact angle was obtained from a captured droplet of colored hexadecane under the membrane in a cuvette filled with the aqueous phase. The results are shown in Fig. 2. For all surfactants and ionic strengths, there is a rather high contact angle, here indicating a rather hydrophilic surface and thus little spreading of the oil droplet.

For SDS, the contact angles are 150 ± 0.5 , 140 ± 0.5 and 131 ± 4 for 1, 10 and 100 mM. There seems to be a slight decreasing trend, indicating increased hydrophobic interactions. Due to the dissociation of OH groups on the cellulose surface it is slightly negatively charged. At higher ionic strengths, the negatively charged droplet might interact more favourably with the negative membrane surface, allowing more spreading of the oil droplet. For CTAB we see a slightly increasing contact angle at increasing ionic strength. The contact angles measured are 148 ± 2 , 149 ± 2 and 151 ± 1 for 1, 10 and 100 mM NaCl respectively. This might indicate an increase in hydrophilic interactions. The cationic surfactant CTAB will adsorb to the negatively charged cellulose. A higher ionic strength could lead to more CTAB adsorption and to the observed slight change in contact angle.

For TX, there is no influence on the contact angle, as the measured values are 148 ± 0.4 , 149 ± 0.4 and 149 ± 0.2 for 1, 10 and 100 mM respectively. This is in line with expectations. Because TX has no charge, we also do not expect an influence of the ionic strength.

Similar behavior is observed for DDAPS. The contact angle was 150 ± 2 , 152 ± 1 and 151 ± 1 for 1, 10 and 100 mM respectively. Just as with TX, we expected no significant influence of the ionic strength on the contact angle, as the head group has no net charge.

4.3. SDS stabilized emulsions

An emulsion with 100 ppm hexadecane, 463 mg/L SDS and 1, 10 and 100 mM NaCl was filtered in a crossflow membrane filtration system using a regenerated cellulose membrane. The crossflow velocity was 0.2 m/s and the transmembrane pressure was kept constant at 1 bar. The flux decline as a function of permeate volume is plotted in Fig. 3. At 1 mM NaCl, the flux decline is gradual, and after three hours of filtration the flux decline reached $50 \pm 3\%$ of the initial flux. At 10 mM NaCl, the initial flux decline is very steep, after which the flux decline becomes more gradual. At the end of the experiment, the flux had dropped to $37 \pm 6\%$ of the original flux. At 100 mM NaCl, the flux first declines quite fast, and then slows down, reaching a permeate flux of $23 \pm 3\%$ of the initial

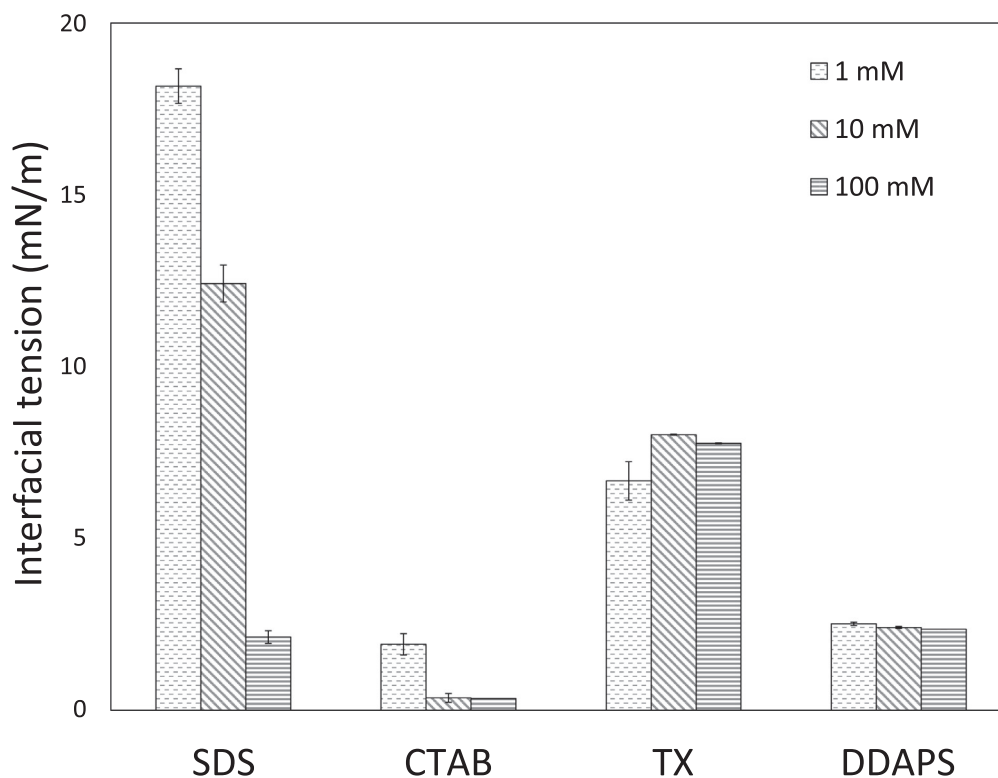


Fig. 1. The interfacial tension of the water/oil interface for four different surfactants and three different salt concentrations as indicated.

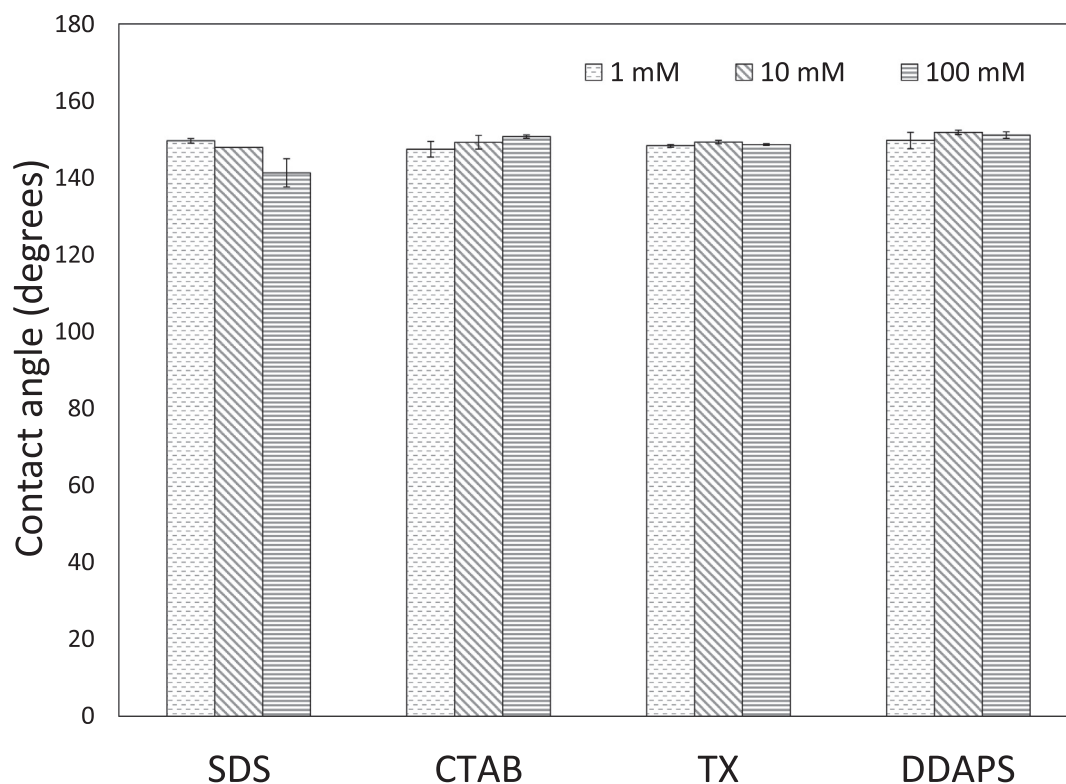


Fig. 2. The contact angle of an oil droplet trapped under the membrane surface in the aqueous phase, for four different surfactants and three different salt concentrations as indicated.

flux at the end of the experiment. From these results, it is clear that increasing the ionic strength has a strong influence on the flux decline, where a higher ionic strength gives more membrane foul-

ing. The initial flux decline is associated with the direct adsorption of oil droplets to the membrane, whereas the more gradual flux decline later on in the experiment is associated with the formation

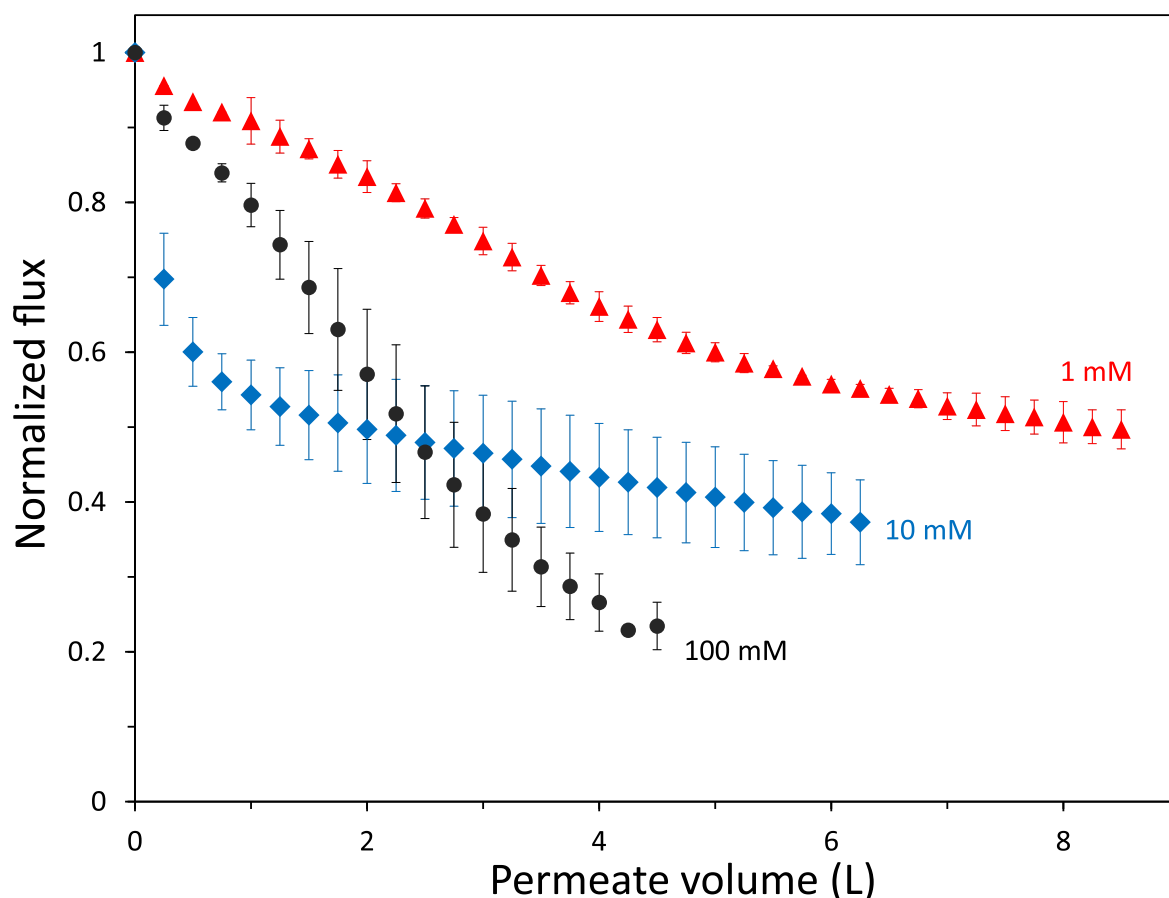


Fig. 3. Flux decline of SDS stabilized emulsions at a crossflow velocity of 0.2 m/s and a transmembrane pressure of 1 bar. Error bars represent standard deviation after duplicates.

of a cake layer [29]. During cake layer formation, however, the interaction between oil droplets dominates. For 1 and 100 mM NaCl, the flux decline follows a similar trend, whereas the flux decline at 10 mM shows a much steeper initial decline. This suggests there is a different fouling mechanism dominating the initial flux decline.

The flux recovery of the membrane was measured after a cleaning procedure including a forward flush, backwash and another forward flush of the membrane cell. The results are given in Table 1. At higher salt concentrations, the flux recovery increases, although we observed that the degree of fouling increases. Two possible mechanisms may be able to explain this observation. Firstly, we expect the cake layer formed on the surface to become denser at high ionic strengths, as a consequence of screening of the charged surfactants at the oil droplets interfaces. A denser cake layer might be easier to remove as a whole, hence the increase in flux recovery at high ionic strengths. In literature, it was observed that larger particles and aggregates are indeed more prone to detach from a cake layer [46]. The second explanation is that at higher ionic strength, more surfactants are adsorbed to the droplet interface, as discussed above. Upon flushing with pure water, the salt and surfactant are diluted and removed from the cake layer, which can have a destabilizing effect. However, because the initial concentration of surfactant was higher at high ionic strengths, the droplets might stay stable for a longer period of time, allowing for easier cleaning.

The oil retention for SDS stabilized emulsions is between 90 and 95 % for all ionic strengths. High retentions were expected based on the theoretical critical pressure (Eq. (6)) required to push an

Table 1

Flux recovery, oil retention and critical pressure at 48 kg/h and 1 bar TMP for SDS stabilized emulsions. The theoretical critical pressure was calculated using Eq. (6), and data from Sections 3.1 and 3.2. The error margin on the flux recovery is an approximation, as the membrane broke during cleaning after several experiments.

Salt concentration (mM)	Flux recovery (%)	Oil retention (%)	Critical pressure (bar)
1	74 ± 8	93 ± 5	10.5
10	78 ± 5	94.5 ± 2.5	7.0
100	95 ± 8	90 ± 6	1.1

oil droplet through the membrane. This was calculated on the basis of the data previously shown and it is for all three ionic strengths predicted to be above the applied pressure of 1 bar. This means that the small amount of oil found in the permeate is probably made up of the smallest droplets present in the feed stream passing through the largest pores in the membrane.

4.4. CTAB stabilized emulsions

The same experimental conditions were used to filter an emulsion containing 100 ppm oil, 346 mg/L CTAB and 1, 10 or 100 mM NaCl. The flux decline upon filtration of CTAB-stabilized emulsions is plotted in Fig. 4. It is immediately apparent that the behavior is different from the results obtained with SDS-stabilized emulsions. The flux decline is much lower for CTAB-stabilized emulsions, reaching a value of $80 \pm 2\%$ for 1 mM NaCl, $84 \pm 1\%$ for 10 mM NaCl and $70 \pm 10\%$ for 100 mM NaCl after three hours of filtration. The

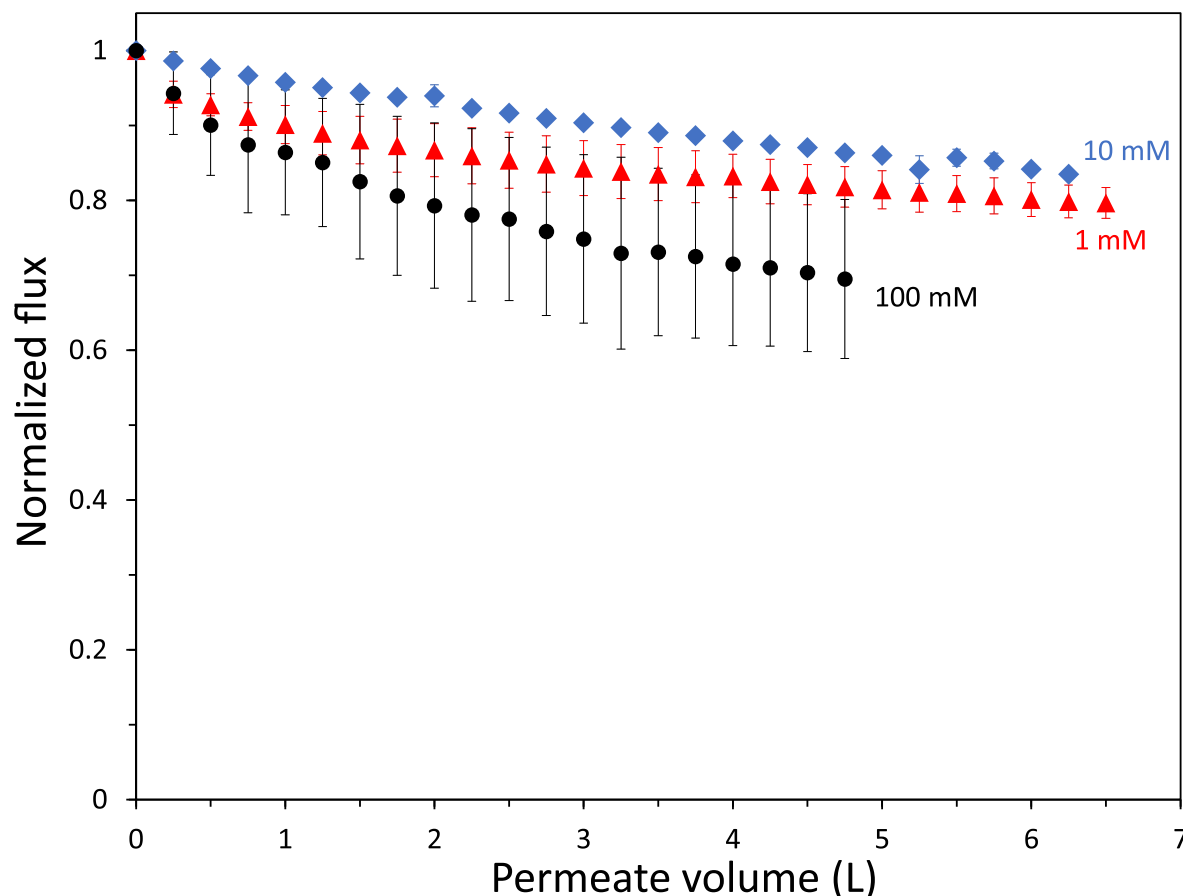


Fig. 4. Flux decline of CTAB stabilized emulsions at a crossflow velocity of 0.2 m/s and a transmembrane pressure of 1 bar. Error bars represent standard deviation after duplicates.

flux decline is gradual for all three ionic strengths and seems to approach a steady value at the end of the filtration experiment.

The flux recovery of CTAB shows no clear trend with increasing ionic strength (Table 2). The values measured for the different experiments vary quite strong even for repetitions, suggesting that removal of this cake layer is sensitive to slight variations in the experiments. We do see however, that at 100 mM NaCl, the flux recovery is high in all measurements. We also see, that for this ionic strength the oil retention is very low as almost all oil passes through the membrane. This means that there is simply not a lot of oil left on the feed side to form a cake layer, possibly also allowing easier cleaning. When we calculate the theoretical critical pressure required to push these CTAB-stabilized oil droplets through the membrane, it is clear that only at 1 mM NaCl we are above the critical pressure. At 10 and 100 mM NaCl, oil would be expected to permeate through the membrane. While this is clearly the case for 100 mM NaCl, the oil retention at 10 mM however is still 89%, despite being filtered above the critical pressure. It seems that with the theoretical critical pressure, as calculated with Eq. (6), we can explain the observed trends. At the same time, it cannot perfectly predict at which ionic strength oil will permeate.

4.5. TX stabilized emulsions

The flux decline of emulsions stabilized with the nonionic surfactant TX at three different salt concentrations is plotted in Fig. 5. As expected, the increase in ionic strength has little influence on the flux decline. After three hours of filtration, the flux

Table 2

Flux recovery, oil retention and critical pressure at 48 kg/h and 1 bar TMP for CTAB stabilized emulsions.

Salt concentration (mM)	Flux recovery (%)	Oil retention (%)	Critical pressure (bar)
1	90 ± 9	95	1.1
10	82 ± 10	89	0.2
100	91 ± 2	3	0.2

has decreased to $23 \pm 1\%$ for 1 mM NaCl, $30 \pm 4\%$ for 10 mM NaCl and $26 \pm 12\%$ for 100 mM NaCl. The nonionic head groups on the droplet surface do not give a surface charge, so there is no electrostatic repulsion between the droplets. This leads to a dense cake layer and therefore more resistance.

The flux recovery for the membrane after filtering TX-stabilized emulsion is in all cases around 80 % (Table 3). This indicates that there is a substantial amount of irreversible fouling. This can be due to a cake layer that is hard to remove, or the fouling takes place in the pores of the membrane in addition to the formation of a cake layer on the surface. The oil retention for TX-stabilized emulsion is below 80% for all ionic strengths (Table 3). The calculated critical pressure is however higher than the applied pressure, suggesting that oil passes through the pores by another mechanism. At sufficient high shear forces, droplets can break up and pass through the membrane [44]. Since oil can pass through the membrane and the flux recovery after forward and back washing is relatively low, the irreversible fouling of the membrane might take place primarily inside of the pores.

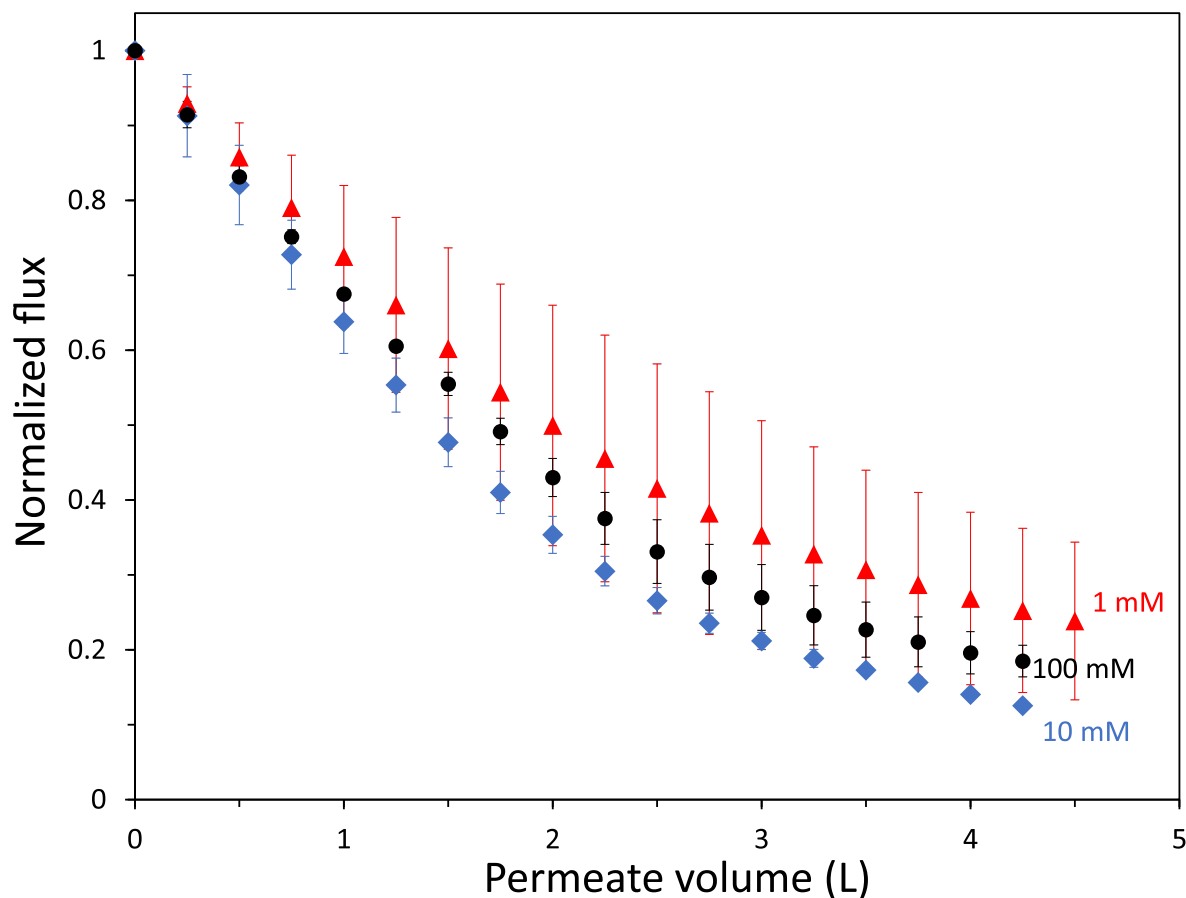


Fig. 5. Flux decline of TX stabilized emulsions.

Table 3

Flux recovery, oil retention and critical pressure at 48 kg/h and 1 bar TMP for TX stabilized emulsions.

Salt concentration (mM)	Flux recovery (%)	Oil retention (%)	Critical pressure (bar)
1	78 ± 11	77 ± 1	3.8
10	80 ± 1	69 ± 4	4.6
100	79 ± 11	74 ± 12	4.5

4.6. DDAPS stabilized emulsions

Finally, we studied the flux decline upon filtration of an emulsion stabilized by the zwitterionic DDAPS. Surprisingly, this surfactant has not been studied as much as the other three surfactants, while the anti-fouling properties attributed to zwitterionic species might make it very relevant for this challenging application. The head group of a zwitterionic surfactant has no net charge, but a positively and a negatively charged moiety. Because of this, it is capable of forming a hydrated layer around the head group. Therefore, we expect it to have excellent antifouling properties, because hydrophobic interactions will be hindered [47]. The flux decline of the membrane filtration experiment at three different salt concentrations is given in Fig. 6. The flux decline after 3 h of filtration is $81 \pm 7\%$ for 1 mM NaCl, $97 \pm 2\%$ for 10 mM NaCl and $95 \pm 1\%$ for 100 mM NaCl. Especially for the higher ionic strengths, the flux decline is so low that either no cake layer forms on the surface, or the cake layer is extremely open. We also noted that the flux

decline decreased at increasing ionic strength. This is line with expectations, as we expect that the stabilizing effect of DDAPS increases with increasing ionic strength [34].

The flux recovery after forward flushing and backwashing is given in Table 4. For all ionic strengths the flux recovery is above 96%, which indicates excellent cleanability. Since there was virtually no flux decline, there is probably not a lot of fouling to remove. The oil retention for DDAPS stabilized emulsions at CMC is also given in Table 4. The oil retention decreases with increasing ionic strength, but it is not completely clear why. There is no evidence from the interfacial tension data that the oil droplets become more deformable at higher ionic strength, neither does the predicted critical pressure change.

The low fouling propensity of the zwitterionic surfactants at high salt concentration is very promising, but the oil retention is much too low. For this reason we further studied the effect of surfactant concentration on both flux decline and oil retention. In Fig. 7, we show flux decline curves for zwitterionic surfactant concentrations of 0.1, 0.2 and 1 times CMC at 100 mM NaCl, while in Table 5 we show flux recovery and oil retention. Decreasing the surfactant concentration to 0.2 CMC translates into a slightly higher flux decline, but strongly increases the oil retention ($85 \pm 6\%$, Table 5). At lower surfactant concentration the oil droplets are less deformable due to a higher interfacial tension (10.5 and 14.1 mN/m respectively for 0.2 and 0.1 times CMC). If we further lower the surfactant concentration to 1/10 CMC, we observe no flux decline over the timescale of our experiment, retaining a high oil retention (85%).

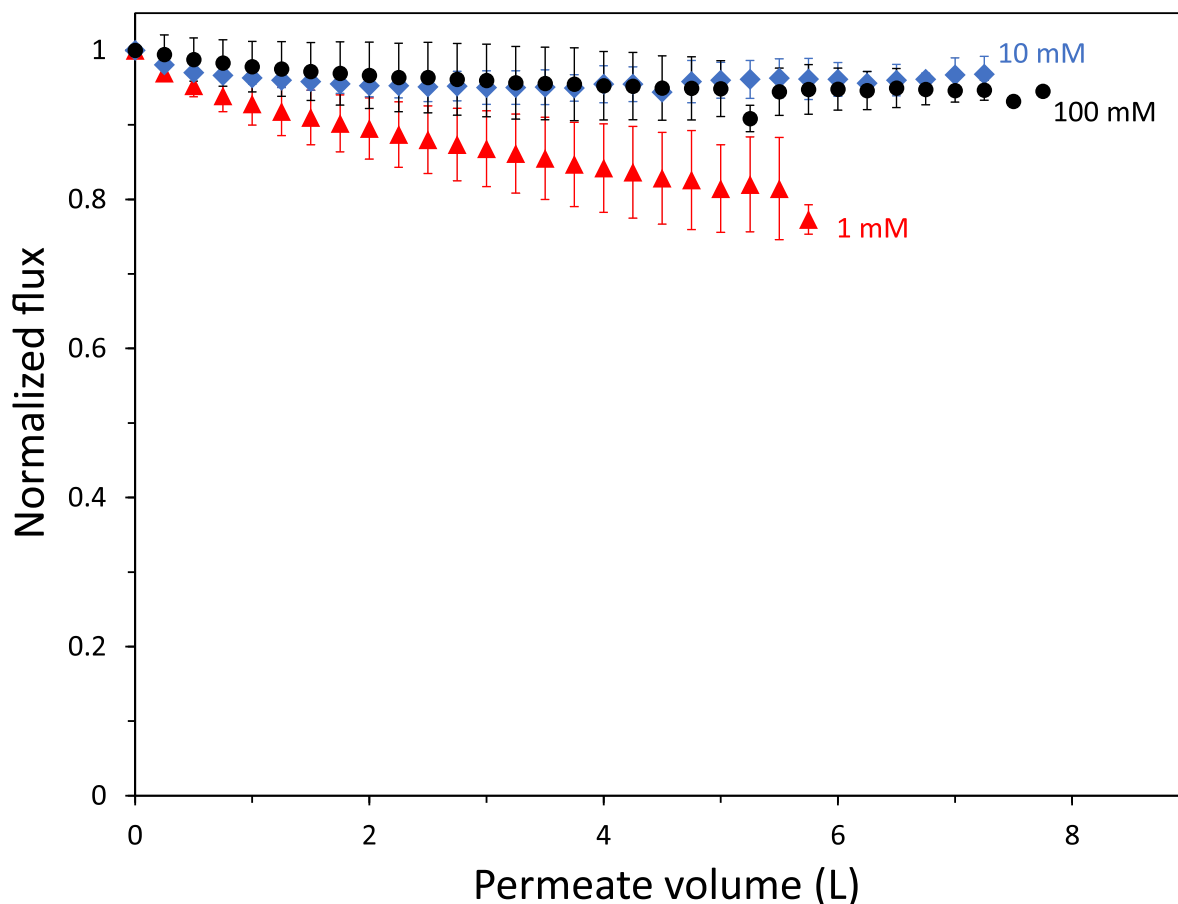


Fig. 6. Flux decline of DDAPS stabilized emulsions.

Table 4

Flux recovery, oil retention and critical pressure at 48 kg/h and 1 bar TMP for DDAPS stabilized emulsions.

Salt concentration (mM)	Flux recovery (%)	Oil retention (%)	Critical pressure (bar)
1	98 ± 2	78 ± 6	1.4
10	96 ± 1	70 ± 20	1.4
100	98 ± 2	44 ± 6	1.4

5. Discussion

In the previous section, we showed results of the membrane filtration of emulsions stabilized with four different surfactants and at 3 different ionic strengths. In our theory Section 1.1, we stated that according to the DLVO theory and the Kozeny-Carman term, we expect that charged surfactants show a change in flux decline with increased ionic strength due to a changing porosity of the cake layer. A higher ionic strength is expected to lead to a lower porosity of the cake layer and thus a higher flux decline. For SDS, an anionic surfactant, this effect was very pronounced, as at higher ionic strength the flux decline was much more severe. For CTAB however, a cationic surfactant, the effect was less pronounced. At higher ionic strength, the oil permeation increased substantially, especially at 100 mM (only 3% oil retention). With more oil permeating, less oil will remain as a fouling layer. The oil permeating, especially at high ionic strength, is in line with the very low interfacial tension (and thus low critical pressure) of CTAB stabilized oil droplets. For surfactants without a head group charge, we expected no or little effect of changing the ionic strength on membrane fouling and flux decline. Indeed for the

non-ionic surfactant TX and the zwitterionic surfactant DDAPS, the observations in membrane filtration were different from those observed for CTAB and SDS. Changing the ionic strength did not have a large effect on the flux decline for both TX and DDAPS, although for DDAPS the flux decline was lower at the higher ionic strengths. The extent of flux decline, however, was very different for these surfactants. Whereas TX stabilized emulsions showed a very strong flux decline, DDAPS stabilized emulsions showed almost none. We propose that this has to do with the different stabilizing mechanisms of the head groups. TX stabilizes by steric hindrance by a long non-ionic head group. As this is a short range interaction (compared to ionic interactions) this leads to a cake layer with a rather low porosity and thus a high flux decline. DDAPS however is a zwitterionic surfactant. The positive and negative moieties on the head group are capable of forming a hydration layer around the oil droplets, providing a very strong inter droplet repulsion. With very low flux declines, especially at higher ionic strengths, it seems that the high repulsion is even able to prevent a cake layer from forming. Such behaviour is in line with the excellent anti-fouling properties normally attributed to zwitterionic headgroups and zwitterionic polymers, especially at increasing ionic strength [33,47]. Furthermore, by tuning the surfactant concentration it is possible to achieve excellent performance. At a low DDAPS concentration, 0.1 CMC, we observed no flux decline and good oil retention (85 %), even at high ionic strength.

As our results show, the type of surfactant can have a large influence on the fouling potential of otherwise identical oil-in-water emulsions. Moreover, the effects of ionic strength are different, depending on the exact type and especially charge of the surfactant. Where charged surfactants stabilize emulsions well

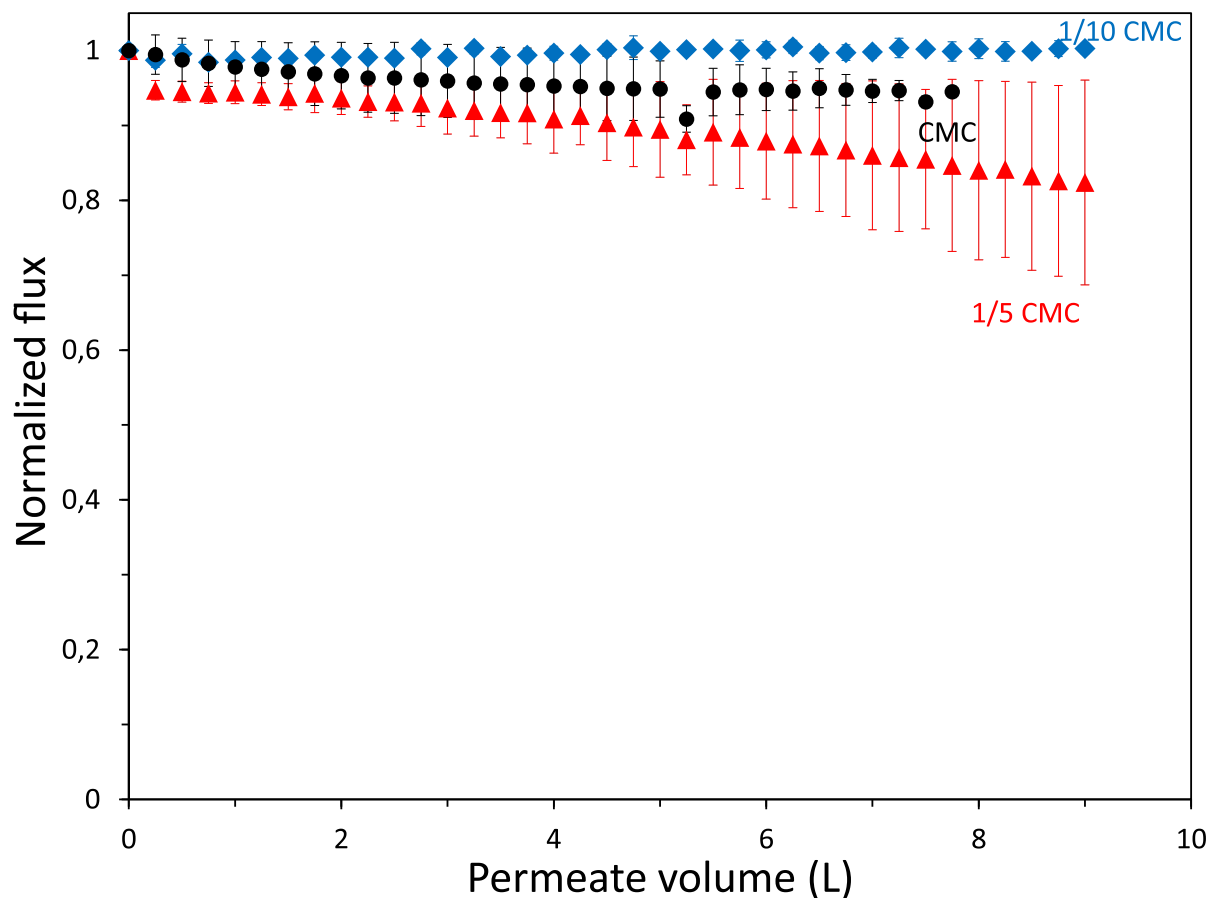


Fig. 7. Flux decline of DDAPS stabilized emulsions as a function of surfactant concentration.

Table 5

Flux recovery and oil retention at 48 kg/h and 1 bar TMP for DDAPS stabilized emulsions.

Surfactant concentration (CMC)	Flux recovery (%)	Oil retention (%)	Critical pressure (bar)
0.1	100 ± 0	85 ± 0	8.1
0.2	99 ± 1	85 ± 6	6.0
1	98 ± 2	44 ± 6	1.4

because of their electrostatic repulsion, factors such as interfacial tension or interactions with the membrane surface definitely play an important role too in determining its appropriateness for membrane filtration and should be considered in the choice of surfactant. Especially at high salt concentrations, often found in produced waters, the use of charged surfactants can either lead to more fouling or to the passing of oil through the membrane. Nonionic surfactants, which are far less influenced by a high salt concentration, did however also not show desirable behavior. Because of a lack of electrostatic repulsion and their short range steric interactions the cake layer becomes far too dense, leading to a high flux decline. The zwitterionic surfactant DDAPS showed excellent performances due to its hydration layer, with no flux decline and 85% oil retention at the highest ionic strength tested (100 mM) and at 0.1 CMC. The zwitterionic headgroup chemistry allows for such low fouling performances while the higher interfacial tension, due to the lower surfactant concentration, maybe responsible for the higher oil retention. These results make DDAPS especially promising for successful treatment of oily waste waters at high salinity, while they are also capable of replacing the surfactants currently used for enhanced oil recovery [48].

6. Conclusion

In this work, we studied membrane fouling by artificial oily waste water for four different surfactant types, all at varying ionic strength. In this way, we demonstrate clearly that the effects of ionic strength on performance parameters such as flux decline, oil rejection and flux recovery after cleaning, are strongly linked to the type of surfactant used. For the anionic SDS, oil is retained well, but the flux decline is much stronger at higher ionic strength. Prolonged filtration leads to the formation of a cake layer at the membrane surface, as shown in previous works [23,24,29]. We hypothesise that, at low ionic strength, strong electrostatic repulsion between SDS stabilized oil droplets leads to the formation of an open cake layer and a relatively low flux decline. But at higher ionic strength the electrostatic repulsion is reduced, leading to denser cake layers and higher flux declines. For the cationic surfactant CTAB, much lower flux reductions are observed including a less pronounced effect of the ionic strength compared to SDS. For CTAB the oil-water interfacial tension at high salt is so low, that the oil droplets can be pushed through the membrane. While at 1 mM of NaCl, 95% of oil is retained, at 100 mM of NaCl, only 3% of oil is retained. For charged surfactants, a high ionic strength can thus lead to denser cake layers, but can also lead to a drop in oil retention. As expected, the effect of ionic strength for the non-ionic surfactant TX, and the zwitterionic DDAPS, are small compared to the effects observed for CTAB and SDS. Still the extend of fouling differs greatly. For TX the flux decline is large (around 80% for all ionic strengths), while for DDAPS low flux decline was observed, especially at higher ionic strengths (>10 mM), with no flux decline at 0.1 CMC and 100 mM NaCl. The highly hydrated

nature of the zwitterionic headgroup makes this surfactant type especially promising for successful oily streams filtration. We see a bright future for zwitterionic surfactants in enhanced oil recovery, but more study needs to be carried out.

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