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Ultrafiltration of saline oil-in-water emulsions stabilized by an anionic surfactant: Effect of surfactant concentration and divalent counterions

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ABSTRACT

The paper presents results of a direct visualization study of membrane fouling by hexadecane-in-water emulsions (0.1% v/v) stabilized by sodium dodecyl sulfate (SDS; 0.1 mM or 3 mM) in the presence of divalent counterions (Mg^{2+}; 0 mM, 6.7 mM, or 42.6 mM). Direct Observation Through the Membrane (DOTM) tests were performed using an ultrafiltration membrane (Anopore; $d_{pore} = 0.02$ µm) and low wettability by hexadecane (contact angle, θ, in 3 mM aqueous solution of SDS is ~164°). Three emulsions employed in DOTM tests had different values of interfacial tension and surface charge and exhibited distinctly different behaviors of oil droplets on the membrane surface. In addition to decreasing the solubility of SDS, $MgSO_4$ had two opposing effects on emulsion stability wherein both interfacial tension and ζ-potential of oil droplets decreased; the overall effect of $MgSO_4$ was a more facile droplet coalescence that was further promoted by permeate flux and concentration polarization of oil. The dominant fouling mechanism was cake filtration with multilayer and sub-monolayer coverages observed for different conditions. Because of the relative oleophobicity of the membrane, the attached oil did not form contiguous oil films. Under conditions of extensive coalescence (high $MgSO_4$), oil droplets reached a critical size and were then removed by the crossflow resulting in minimal membrane fouling.

1. Introduction

Oil-in-water emulsions represent a major waste stream of oil and gas, metal finishing, mining and other industries. The efficiency of commonly used oil-water separation technologies decreases dramatically with a decrease in oil droplet size; for example, hydrocyclone separation becomes ineffective when the droplet size decreases below ~10 µm [1]. Yet, the amount of oil contained in small droplets can be sufficiently high to necessitate their removal to meet regulations on the maximum allowable concentration of oil in the discharge [2]. Membrane filters can remove small oil droplets and offer a viable alternative for treating oil-in-water emulsions [3]. Membrane fouling, however, remains a challenge especially when treating complex feeds such as flowback and produced water [4,5] with their multicomponent and dynamically changing composition [6]. Most produced waters are saline or brackish [7] and elevated salinity in such feeds presents additional challenges for membrane separations. First, salt removal, if required, raises the cost of treatment. Second, when present in sufficiently high concentration, the salt can alter stability and other properties of oil-in-water emulsions possibly leading to increased membrane fouling. A number of studies have evaluated nanofiltration and reverse osmosis as treatment options for produced water (e.g. [8,9]).

Surfactants are typically employed to stabilize emulsions. Sodium dodecyl sulfate (SDS) is a commonly used anionic surfactant and as such should interact strongly with divalent cations such as Ca^{2+} and Mg^{2+} that can be present in natural waters in high concentrations. Typical concentrations in groundwater and surface water range from ~1–50 mg/L for Mg^{2+} and from ~1–200 mg/L for Ca^{2+} [10]. In seawater, the concentrations of Mg^{2+} and Ca^{2+} are 1350 mg/L and 400 mg/L, respectively [11]. Pore space brines brought to the surfaces during hydraulic fracturing may have much higher concentrations yet. For example, analyses of brines from a range of geologic environments in western Pennsylvania yielded Mg^{2+} and Ca^{2+} concentrations of 4150 mg/L and 41,600 mg/L, respectively [12].

Nanofiltration and reverse osmosis membranes reject these cations leading to even higher concentrations in the vicinity of the membrane surface where the ions can interact with other rejected dissolved or particulate species such as colloids and oil droplets. The resulting concentration polarization may cause precipitative fouling of the

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membrane by inorganic compounds with low solubility products (e.g., $Mg(OH)_2$, $CaCO_3$, $CaSO_4$). Scaling of sparingly soluble salts leads to a dramatic decrease in permeate flux due to precipitative fouling [13]. Further, in the presence of salts the adsorption behavior of surfactants changes [14], which can translate into differences in membrane fouling [15]. At sufficiently high salinities, critical micelle concentration is exceeded, which can modify fouling behavior of surfactant-stabilized emulsions [16]. Finally, dissolved ions alter the interfacial tension of emulsions. For example, Adamczyk et al. observed a significant reduction in surface tension for an aqueous solution of cetyltrimethylammonium bromide (CTAB) with an increasing concentration of KCl in the solution [17].

Currently, the largest drawback to membrane-based treatment of oily wastewaters is membrane fouling and the subsequent costs associated with cleaning and replacing the membranes. Fouling mitigation methods include hydraulic cleaning (e.g., water flushes and water back flushes), chemical cleaning, and mechanical cleaning (e.g., air back pulses, ultrasound, vibrational cleaning, and sponges sent through the interior of tubular membranes). Membrane cleaning is costly in terms of time and money as the treatment must be temporarily stopped, costs for chemicals and their disposal, and significant capital investments for equipment. When irreversible fouling decreases permeate flux below a certain threshold value, the membrane modules have to be replaced. Understanding membrane fouling by oil can help with the development of new membrane materials and operational approaches to better mitigate fouling and reduce cleaning costs. Yet surprisingly little is known about the formation dynamics and structure of the fouling layer formed on the membrane surface by emulsified oil [18].

Minimizing droplet deposition on the membrane surface by hydrodynamic means is one strategy for decreasing membrane fouling. For droplets that do deposit on the membrane, preferred behaviors can be promoted to avoid egregious forms of membrane fouling such as complete blocking [19] of individual pores or formation of a contiguous film of oil that “seals” large areas of the membrane surface. For relatively unstable droplets, a preferred scenario would involve surface coalescence with other attached droplets to reach a critical size when the resulting larger droplet is swept off the membrane by crossflow [18]. For more stable emulsions, a preferred scenario might be the formation of relatively thin and permeable layer of oil droplets that can be easily removed by a hydraulic flush. Sufficient stability would ensure that droplet deformation is minimal to avoid low porosity cakes. Electrostatic forces may become more important (relative to hydrodynamic interactions) for smaller droplets expected in stable emulsions; under these conditions higher electrical charge on oil droplets would help minimize oil accumulation at the membrane surface and would facilitate membrane cleaning. Whichever fouling scenario unfolds, droplet coalescence is a critical process that determines in part the rate and extent of membrane fouling.

Coalescence of surfactant-stabilized droplets in a membrane filtration system can occur both in the bulk of the feed emulsion and at the membrane surface. Coalescence can be viewed as a result of a sequence of several events:

1) Long-range transport of droplets that brings them into close proximity to one another. This transport is governed by hydrodynamic forces and long-range (>5 nm) droplet-droplet and droplet-membrane interactions [20]. In the classical flocculation theory, this step is described by collision frequency [21].
2) Droplet adhesion that results from an attractive force between droplets overcoming short-range repulsion due to surface-associated surfactants. The droplets are separated by a very thin liquid film stabilized by surfactant layers. The solubility of the surfactant [22–24] and, as a consequence, the ionic makeup of the dispersion media, play an important role in droplet stability. The time that the droplets reside in a close proximity to one another, $t_{contact}$, can be limited by droplet removal from the surface or by droplet coalescence. In the classical flocculation theory this step is described by collision efficiency (also called “attachment efficiency” or “sticking coefficient”), defined as the fraction of particle-particle (or droplet-droplet) contacts that result in attachment (or adhesion).
3) Drainage of the thin film that separates the attached droplets. If the film drains over a period of time, $t_{drainage} < t_{contact}$, and ruptures, coalescence occurs. There are several approaches to describing the probability of coalescence [25], with the film drainage model [26,27] being most commonly used. The model predicts that the coalescence efficiency is given by

$$\lambda = exp\left(-\frac{t_{drainage}}{t_{contact}}\right) \tag{1}$$

The drainage occurs differently depending on whether the droplets are deformable and whether their interfaces are mobile [25]. In the case of deformable particles with partially mobile interfaces, drainage time is given by [28]:

$$t_{drainage} = \frac{\pi\mu F^{1/2}}{2(2\pi\sigma/r_{drop})^{3/2}}\left(\frac{1}{h_f} - \frac{1}{h_i}\right) \tag{2}$$

where σ (N m^{-1}) is interfacial tension, h_i and h_f are initial and critical film thickness (m), μ is the dynamic viscosity of oil (Pa s), r_{drop} is droplet radius (m), and F is the compressive force (N).

The structure of the oil fouling layer as it develops on the membrane surface during the separation of an oil-in-water emulsion is not fully understood. Mechanistic dead-end filtration studies have described the oil deposit as a highly compressible gel layer or a “cake” based on the expression derived for spherical, non-deformable particles. Our previous work [18] described the first application of a direct visualization technique - Direct Observation Through the Membrane (DOTM) - to capture real-time images of a membrane surface under conditions of fouling by emulsified oil in the presence of crossflow. This previous study employed a microfiltration membrane (Anopore, 0.2 µm nominal pore size) and hexadecane-in-water emulsions stabilized by SDS (0.1 mM, or 0.4 mM, or 0.8 mM) and revealed three characteristic stages of membrane fouling: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence followed by removal of droplets larger than a critical size. In that study, the emulsion was prepared by adding hexadecane and the surfactant to DI water with no other ions present in the dispersion phase. The observed stages of membrane fouling can be mapped by the steps leading to droplet coalescence in a straightforward manner. Droplet attachment and clustering corresponds to the long-range transport of droplets to the membrane surface and initial adhesion of droplets to one another. Droplet deformation corresponds to continual adjustment of droplet-droplet and droplet-membrane contact lines in response to the changing compressive (i.e. drag) force and crossflow shear. The dynamics of the three-phase contact line is affected by initial conditions such as the kinetic energy of the attaching droplet [29]. The third stage – coalescence – is affected by the presence of the membrane. Coalescence of sessile droplets is different from the free droplet coalescence in at least two aspects. First, attachment to the membrane surface extends droplet residence time, $t_{contact}$, in the vicinity of other attached droplets, which according to Eq. (2) should facilitate droplet-droplet coalescence. At the same time, the membrane imposes surface viscous stresses on attached droplets, which should hamper the coalescence process. In general, the lower the contact angle is (i.e. the more wettable by oil the surface is), the more significant the deviations in coalescence dynamics are expected to be with respect to those in bulk emulsions. Ionic composition of the background electrolyte can play an important role in defining droplet-droplet and droplet-membrane interactions, coalescence of droplets, and, ultimately, membrane fouling by emulsified oil.

This study examines the effects of an anionic surfactant and divalent