



# Assessment of oil fouling by oil-membrane interaction energy analysis

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## ABSTRACT

Membrane-filtration is promising for treating the voluminous oily wastewater, especially when the oil emulsions are smaller than 20  $\mu\text{m}$ . However, studies on the inevitable membrane fouling phenomenon by oil are rather scarce. In particular, a question that remained to be addressed was whether the DLVO or XDLVO model provides better predictions of the oil-membrane interfacial interactions and thereby the extent of fouling. Accordingly, this study investigated four oil types (namely, hexadecane, soybean oil, fish oil and crude oil) that were stabilized by the same non-ionic surfactant (namely, Tween 20) and had similar mean droplet diameters. The direct observation through the membrane (DOTM) technique was used to quantify the critical flux of the different emulsions, and both the XDLVO and DLVO models were used to quantify the foulant-membrane and foulant-foulant interactions. DOTM results indicated that the critical flux values were similar for all oils under the conditions tested, except crude oil. Although the XDLVO model appears to be more comprehensive than the DLVO in terms of accounting for the additional Lewis acid-base polar (AB) interaction that is acknowledged to be important in membrane-filtration, results indicate that the dominance of the AB component drowns out the other interactions like that of electrostatics (EL) in this case, which impedes accurate prediction of the different fouling tendencies by the different oil types.

## 1. Introduction

Due to the simplicity in operation, high oil removal capability, smaller footprint, and lower capital and operational costs [1,2], membrane technology is a promising method for treating the large volumes of oily wastewater found in the oil and gas, food processing, and metal processing industries [3]. Particularly for oil emulsions smaller than 20  $\mu\text{m}$ , conventional technologies such as gravity-based, hydro-cyclone, centrifugation or dissolved air floatation (DAF) become inefficient in separating oil from water [2], which makes it challenging to satisfy the regulations governing discharge into the environment [4]. As with all membrane-filtration processes, membrane fouling is a major drawback impeding the more widespread use of membrane-based separation systems. This necessitates more mechanistic understanding dedicated to the membrane fouling phenomena by oil emulsions, which are distinct from other particulate foulants in terms of deformation and coalescence [5].

The experimental study of fouling has benefited remarkably from techniques that allow for non-intrusive, real-time observation of the evolution of the fouling phenomenon. Such techniques have only recently been applied to oil emulsions. In particular, the Direct Observation through the Membrane (DOTM) method has been used for

revealing various fouling behaviors by oil-in-water emulsions. Tummons et al. [5] unveiled three characteristic stages of membrane fouling, namely, (1) droplet attachment and clustering, (2) droplet deformation, and (3) droplet coalescence. Oil deformability has also been visualized via a microscope to impact filtration performance [6], and also via the Optical Coherence Microscopy (OCT) to cause internal pore fouling even when the oil emulsions were two orders-of-magnitude larger than the pore [7]. Subsequently, DOTM showed that the effect of salt was such that it not only decreased the solubility of the surfactant, but also decreased the interfacial tension and zeta potential of the oil emulsion, resulting in increased coalescence and thereby larger droplets that are easily sheared off by cross-flow [8]. Tanudjaja et al. [9] then quantified using DOTM the effect of oil concentration, cross flow velocity (CFV) and salinity on the critical flux of oil emulsions. It was also found that the shear-induced diffusion model [10] did not predict well for oil emulsions due to the highly oleophobic membrane used, which suggests expectedly the need to account for interfacial interactions on top of the hydrodynamic effects [11].

As with other foulants, the oil-membrane interaction is one of the determinant factors affecting the extent of fouling [9,12,13]. To this end, the Derjaguin-Landau-Verwey-Overbeek (DLVO) model, which consists primarily of the Lifshitz – van der Waals (LW) and electrostatic

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double layer (EL) interactions, is popularly used to elucidate the interfacial interactions [14–16]. Particularly for membrane-filtration applications, because of the acknowledged dominance of the Lewis acid-base polar (AB) component, the extended DLVO (XDLVO) model thus consists of this additional component [16–19]. Brant and Childress [20] compared the predictions by the classical DLVO theory (i.e., consists only of LW and EL interactions) against that of the XDLVO theory (i.e., consists of LW, EL and AB interactions), and found that the classical DLVO theory indicated that all the foulant-membrane combinations investigated had weak attractions and thereby similar fouling tendencies, whereas the additional AB interactions considered in the XDLVO approach led to marked differences in the total interaction energies. Also, Ahmad et al. [21] showed that the DLVO and XDLVO models provide good explanations as well to the fouling by non-rigid particulate foulants, namely, algae, during microfiltration. In another study, Kühnl et al. [22] experimentally studied the fouling of milk components in the microfiltration (MF) system at various pH values, and found that the flux reduced at lower pH values due to the less repulsive interaction between the casein constituent and the membrane surface, as also quantified by the XDLVO model. Because the hydrophobic and hydration effects represented by the Lewis acid-base (AB) interactions [23–25] are significant for the hydrophobic surfaces in water [23,24] in membrane-filtration applications, the XDLVO model has become increasingly popular relative to the classical DLVO model in membrane-filtration studies. Surprisingly, in a recent study, He et al. [14] reported that, due to the apolarity of crude oil, the DLVO model sufficed to explain the interaction of crude oil emulsion with PVDF membrane at various salt concentrations. This interesting result on oil emulsions that appears to counter previous fouling studies that tend towards XDLVO theory warrants a closer look.

To contribute towards an enhanced mechanistic understanding of membrane fouling by oil emulsion and address the question regarding the relevance of the AB interactions for apolar oil foulants, this study investigated four oil types (namely, hexadecane, soybean oil, fish oil and crude oil) that were stabilized by the same non-ionic surfactant (namely, Tween 20) and had similar mean droplet diameters. Tween 20 was chosen as the surfactant due to its non-ionic nature, thus it did not give additional charge on the oil droplet's surface. Oil concentrations in the range of 250–750 ppm and crossflow velocities in the range of 0.1–0.4 m/s were studied. The direct observation through the membrane (DOTM) technique was used to quantify the critical flux of the different emulsions, and both the XDLVO and DLVO models were used to quantify the foulant-membrane and foulant-foulant interactions. The agreement or lack thereof of the experimental results and predictions by the two models were assessed and discussed.

## 2. Theory

### 2.1. DLVO and extended DLVO (XDLVO)

The classical DLVO theory states that the total interaction energy is the sum of the Lifshitz-van der Waals (LW) and electrostatic (EL) components, with the Brownian (BR) component negligible for the micron-sized foulant considered here:

$$U_{mlo}^{DLVO} = U_{mlo}^{LW} + U_{mlo}^{EL} \quad (1)$$

where  $U_{mlo}$  denotes the interaction energy between the membrane and the oil emulsion, with the subscripts  $m$ ,  $l$  and  $o$  denote respectively the membrane, liquid environment in the bulk feed and oil emulsion. On the other hand, the extended DLVO theory stipulates an additional polar Lewis acid-base (AB) component [26]:

$$U_{mlo}^{XDLVO} = U_{mlo}^{LW} + U_{mlo}^{EL} + U_{mlo}^{AB} \quad (2)$$

#### 2.1.1. LW interaction

The LW (Lifshitz-van der Waals) interaction energy represents the non-polar interaction between two surfaces, specifically in this case between the membrane and oil emulsion, which can be expressed as the free energy of adhesion per unit area ( $\Delta G^{LW}$ ) between two infinite planar surfaces [16]:

$$\Delta G_{y_0}^{LW} = 2(\sqrt{\gamma_l^{LW}} + \sqrt{\gamma_m^{LW}})(\sqrt{\gamma_o^{LW}} + \sqrt{\gamma_l^{LW}}) \quad (3)$$

where  $\gamma$  denotes the surface tension (i.e., surface free energy per unit area) of a medium (i.e., liquid or membrane or oil), and the subscript  $y_0$  denotes the minimum separation distance of the two surfaces and is usually assigned the value of 0.158 nm [14,16]. According to Brant and Childress [16], in order to get the actual interaction energy between the membrane surface (assumed to be an infinite planar surface) and oil droplet (assumed to be a sphere), the Derjaguin's technique can be applied to scale the interaction energy to a required geometry. By applying this technique, the LW interaction energy as a function of separation distance ( $h$ ) between the membrane and oil emulsion is expressed as:

$$U_{mlo}^{LW}(h) = 2\pi \Delta G_{y_0}^{LW} \frac{y_0^2 a_c}{h} \quad (4)$$

where  $a_c$  is the radius of the oil droplet.

#### 2.1.2. EL interaction

The EL interaction is a function of the electrostatic or the zeta potential, and the free energy per unit area ( $\Delta G^{EL}$ ) between two infinite planar surfaces is given by [16]:

$$\Delta G_{y_0}^{EL} = \frac{\varepsilon_0 \varepsilon_r \kappa}{2} (\zeta_m^2 + \zeta_o^2) [1 - \coth(\kappa h) + \frac{2\zeta_m \zeta_o}{(\zeta_m^2 + \zeta_o^2)} \operatorname{csch}(\kappa h)] \quad (5)$$

where  $\zeta_m$  and  $\zeta_o$  are the zeta potentials of respectively the membrane and the oil,  $\varepsilon_0 \varepsilon_r$  is the dielectric permittivity of the liquid environment,  $\kappa$  is the inverse Debye screening length and is equal to 1  $\mu\text{m}$  for DI water [27]. By applying the Derjaguin's technique, the EL interaction energy as a function of the distance between the membrane surface and oil droplet can be obtained by:

$$U_{mlo}^{EL}(h) = \pi \varepsilon_0 \varepsilon_r a_c [2\zeta_m \zeta_o \ln\left(\frac{1+e^{-\kappa h}}{1-e^{-\kappa h}}\right) + (\zeta_m^2 + \zeta_o^2) \ln(1-e^{-2\kappa h})] \quad (6)$$

#### 2.1.3. AB interaction

The AB interaction is the polar interaction due to the electron-donor and electron-acceptor relationship, and the free energy of adhesion per unit area between two infinite planar surfaces is expressed as a function of the polar components of the surface tension of the membrane ( $m$ ), bulk feed solution ( $l$ ), and oil droplet ( $o$ ):

$$\Delta G_{y_0}^{AB} = 2\sqrt{\gamma_l^+}(\sqrt{\gamma_m^-} + \sqrt{\gamma_o^-} - \sqrt{\gamma_l^-}) + 2\sqrt{\gamma_l^-}(\sqrt{\gamma_m^+} + \sqrt{\gamma_o^+} - \sqrt{\gamma_l^+}) - 2(\sqrt{\gamma_m^+ \gamma_o^-} + \sqrt{\gamma_m^- \gamma_o^+}) \quad (7)$$

where the superscripts + and - represent the electron-donor and electron-acceptor. By applying the Derjaguin's technique, the AB interaction energy as a function of separation distance ( $h$ ) between the membrane and oil emulsion is expressed as:

$$U_{mlo}^{AB}(h) = 2\pi a_c \lambda \Delta G_{y_0}^{AB} \exp\left[\frac{y_0 - h}{\lambda}\right] \quad (8)$$

where  $\lambda$  is the characteristic decay length of the AB interaction in water and the commonly used value for aqueous medium is 0.6 nm [28].

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