Understanding membrane pore-wetting in the membrane distillation of oil emulsions via molecular dynamics simulations

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A B S T R A C T

The escalating volume of oily wastewater, particularly produced water, necessitates efficient means of treatment for the recovery of both the water and oil constituents. Towards this end, membrane distillation (MD) is a promising candidate. Unfortunately, studies on the MD of oil emulsions are scarce, in large part because of membrane pore-wetting issues, which undermines the separation of oil and water. An earlier experimental study has indicated that membrane pore-wetting is caused by the presence of surfactant (namely, SDS) and salt (namely, NaCl), rather than oil, but the mechanisms underlying the poor performance remains unknown. Therefore, in order to improve the feasibility of MD, this molecular dynamics study is targeted at revealing the complex interactions that are detrimental to MD performance. The interactions of the three key constituents in produced water (namely, surfactant, oil and salt) among themselves and with the membrane are studied. The worst membrane pore-wetting experimentally observed for feeds containing SDS and NaCl is because NaCl increased the SDS-PVDF affinity without decreasing the mobility of SDS, and thereby leads to decreased surface tension and the increased likelihood of exceeding the liquid entry pressure (LEP). Accordingly, in order to mitigate pore-wetting in the membrane distillation of such feeds, means towards reducing the surfactant-membrane affinity, rather than oil-membrane affinity, and surfactant mobility near the membrane are recommended.

1. Introduction

Produced water represents a significant volume of oily wastewater, among others from for example the food and beverage industry and the shipping and maritime industry, that needs to be adequately treated from both environmental (i.e., prior to disposal and reuse/recycle water) and economic (i.e., recover the oil and water management) perspectives. Towards this end, various methods like gravity separation, hydrocyclones, gas flotation and adsorption are available, each with its unique set of limitations. Particularly for micrometer-sized oil emulsions, membrane-based filtration is a promising technique [1,2]. Other than the more widely used microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membrane-based separations, membrane distillation (MD) is a burgeoning green technology that can efficiently utilize waste heat to enable the separation [3–5].

Studies on fundamentally understanding the MD process for treating oily wastewater are scarce. Gryta and Karakulski [6] found expectedly a negative correlation between flux and crude oil concentration (without surfactants), and that higher oil concentrations led to membrane pore-

wetting and thereby reduced permeate quality. This has been attributed to the reduced partial pressure due to the presence of crude oil and the affinity between the hydrophobic oil and hydrophobic membrane. Another study [7] indicated that using surfactants with a lower hydrophilic-lipophilic balance (HLB) value decreased the adsorption of oil droplets on the membrane surface and thereby mitigated fouling. The surfactant properties are important not only in terms of surfactant-oil interaction (i.e. oil emulsion stability) but also surfactant-membrane interaction. Chen et al. [8] reported stable MD performance of superhydrophobic polyvinylidene fluoride (PVDF) membranes for feeds containing oil-in-water emulsions when anionic surfactant was present, but decreasing performance in the presence of cationic surfactant. They related this performance reduction or pore-wetting of the MD membranes with the electrostatic attraction between the positively charged surfactant and the negatively charged membrane surface. Our recent study [9] indicated surprisingly that neither the oil nor the surfactant (alone or combined) affected the MD performance, but the concurrent presence of sodium chloride (NaCl) and the anionic surfactant sodium dodecyl sulfate (SDS) that severely deteriorated the MD performance. Other studies on hybrid membrane-filtration processes involving MD

have also been reported. El-Abbassi et al. [10] suggested that the integrated microfiltration (MF) - MD is a good combination for the treatment of produced water [10]. Zhang et al. [11] proposed the hybrid forward osmosis (FO) - MD gave good performance with at least 90% feed water recovery. What remains amiss is the cause of pore-wetting, the knowledge of which would help to formulate strategies towards the practical implementation of MD for oily wastewater treatment.

Molecular dynamics simulations have served to shed some light on the complex interactions existing in the oil-surfactant-salt-membrane-water system. Darvishi and Foroutan [12] revealed the importance of positively and negatively charged nano-domains present on the PVDF membrane surface, which affects the positioning and orientation of the water molecules, and hydrophobic and oleophilic nature of the PVDF surface [12]. Meconi et al. [13] investigated the adsorption and desorption behavior of surfactants onto the membrane surface, and proposed that attractive force and concentration have counteracting effects for nonionic surfactants, but similar effects for ionic surfactants [13]. In addition, Li et al. [14] suggested that high salt concentrations (1 M) slightly increases the binding free energy of SDS on a methyl methacrylate (MMA) membrane surface due to the low solubility of SDS tails in salt solutions. However, to date, a systematic understanding on which constituent of produced water causes membrane pore-wetting is lacking.

To bridge the gap in the knowledge base with regards to the mechanisms underlying pore-wetting in MD during the treatment oil emulsions, the key objective of the current molecular dynamics study is to understand the inter-species and species-membrane interactions of the key components in produced water, namely, oil, surfactant (namely, SDS) and salt (namely, NaCl). Through this effort, the mechanisms underlying the detrimental MD performance caused by the concurrent presence of SDS and NaCl observed in our previous experimental study [9] are sought, in order to recommend means to improve the feasibility of MD for treating produced water.

2. Model and molecular simulation setup

Fig. 1 displays the chemical structures of the molecules involved in this study, namely, polyvinylidene fluoride (PVDF) polymer (with five repeat monomer units), hexadecane, sodium dodecyl sulfate (SDS), chloride ion (Cl^-), sodium ion (Na^+) and water. The forcefield
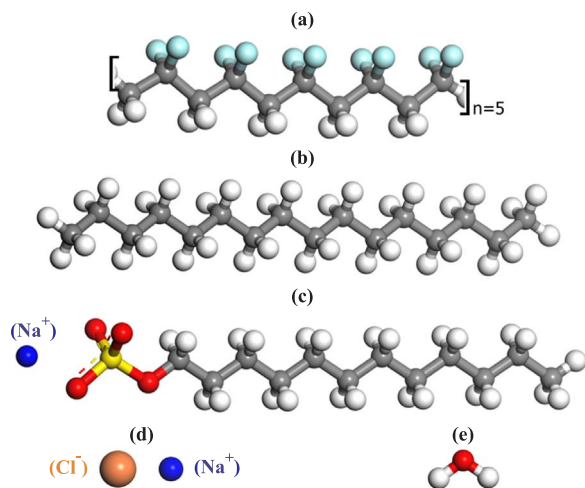

Fig. 1. Chemical structures of (a) polyvinylidene fluoride (PVDF) polymer chain with five repeat monomer units, (b) hexadecane (i.e., oil), (c) sodium dodecyl sulfate (SDS), (d) Cl^- and Na^+ ions, and (e) water. Oxygen, carbon, sulfur, sodium, chlorine, fluorine and hydrogen atoms are represented respectively by red, grey, yellow, blue, orange, cyan and white colors. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

potential parameters of the polyvinylidene fluoride (PVDF; Fig. 1(a)) are adopted from Lachet et al. [15], which are compatible with the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) [16] framework. The forcefield parameters for hexadecane (Fig. 1(b); hereafter referred to as oil), and sodium (Na^+) and chloride (Cl^-) ions (Fig. 1(d)) are adopted from OPLS-AA [16]. The non-bonded and bonded potential parameters of the sodium dodecyl sulfate (SDS; Fig. 1(c)) are adopted from Chun et al. [17] and Tang et al. [18], respectively, which are compatible with the OPLS-AA [16] framework. For the water molecules (Fig. 1(e)), the extended simple point charge (SPC/E) model [19] is used.

All molecular dynamics simulations are carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [20], and analyses and molecular visualization are performed with Visual Molecular Dynamics (VMD) [21] packages. The sequence of key steps is presented in Fig. 2.

Initially, in order to create a flat substrate PVDF to represent the membrane, 38 PVDF polymer chains each consisting of five repeat monomer units (Fig. 1(a)) are placed in the simulation box. The upper wall of the simulation box is descended gradually onto the lower wall of the simulation box until the two walls are a distance of 10 Å apart. This process is conducted within 5 ns in the NVT ensemble with a time step of 0.5 fs. The final configuration of the PVDF confined layer is a flat square with sides (i.e., x and y directions) of ~ 34 Å and a thickness (i.e., z direction) of ~ 10 Å. The final PVDF structure is magnified to obtain a large surface area by multiplying by three in x and y directions, and therefore includes a total number of 342 PVDF chains and has lengths of 101 Å in the x and y directions. Notably, the width and thickness of the polymer slab are consistent with other molecular dynamics simulation studies in the literature used to investigate the adsorption of various species on polymeric membranes [12–14]. Using this forcefield model, a value of 1.75 kg/m³ is obtained for the density of the PVDF membrane, which agrees well with the experimental value of 1.78 kg/m³. Fig. 3(a) shows the top view of the PVDF surface generated, with the different colors reflecting the volume-based partial charge distribution. Fig. 3(b) and (c) further show the charge distribution around respectively hexadecane (i.e., oil) and SDS, with the colors representing the charge distribution around hexadecane and the hydrophobic tail group of SDS being white and grey because of zero partial charge, while the hydrophilic head group exhibits negative partial charge.

The initial configurations of the simulations are generated using the Packmol software [22]. The PVDF surface layer is solvated in a periodic box with 45,000 SPC/E type water molecules [19]. A water layer with a thickness of 100 Å replaces the top PVDF layer. Depending on the targeted test condition, the SDS concentration is varied by adding 3 or 6 molecules (3.7 and 7.4 mM, respectively), and oil and NaCl concentrations are fixed respectively at 800 ppm and 10 g/L as per our previous experimental study [9]. Where present, the number of water and oil molecules are 45,000 and 3, respectively, and the number of Na^+ and Cl^- ions are equal at 138 each. The cut-off distance of 18 Å for non-bonded interactions is adopted. Long-range electrostatics is treated by the PPPM Ewald method. Bond distances involving hydrogen atoms in water are constrained using the SHAKE algorithm. Temperature is maintained at the targeted value by the Nosé–Hoover thermostat with a coupling time constant of 100 fs, while pressure is maintained at 1 bar by the Nosé–Hoover barostat with a coupling time constant of 500 fs. The simulation time step is set to 1 fs.

The system is initiated by bringing the species (i.e., either SDS or oil) to a distance of 20 Å from the surface of the PVDF membrane to investigate if they prefer to attach to or detach from the PVDF surface. The 20 Å distance is an optimized value based on a shorter distance biasing the species to interact with the PVDF rather than water, while a longer distance results in a longer time required for the species to interact with the PVDF. For each system, the SDS and/or oil molecules are positioned 50 Å from one another and centered on the PVDF surface,