



Effects of surfactant properties on pore wetting of membrane distillation

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ABSTRACT

Pore wetting is a major constraint to the performance of membrane distillation (MD) for hypersaline brine treatment. Despite the existence of surfactants with diverse properties, an explicit relationship between the properties of surfactants and their capabilities of inducing pore wetting has yet to be established. In this study, we perform a comparative analysis of the wetting behaviors of various surfactants with different charges and molecular weights in MD desalination. The induction time of surfactants to initiate pore wetting was correlated to the apparent contact angle and surface tension of the feedwater. Our results show that different surfactants resulting in similar feedwater surface tensions can lead to drastically different wetting potential, suggesting that both charge of the head group and molecular weight of surfactants have a significant influence on membrane pore wetting. Further, we demonstrate that parameters that have been commonly used to indicate wetting potential, including apparent contact angle and solution surface tension, are not reliable in predicting the wetting behavior of MD membranes, which is intricately linked with surfactant properties such as charge and molecular size. We envision that our results not only improve our fundamental understanding of surfactant-induced wetting but also provide valuable insights that necessitate thorough consideration of surfactant properties in evaluating wetting potential and membrane wetting resistance for MD desalination.

1. Introduction

In recent years, membrane distillation (MD) has emerged as a promising technology for hypersaline brine treatment. The advantages of MD include its exceptional tolerance to high salinity, nearly perfect rejection of inorganic ions and non-volatile contaminants, the capability of leveraging low-grade thermal energy, and the potential for valuable resource recovery (Deshmukh et al., 2018; Horseman et al., 2021). For example, MD has a great potential for the treatment of hypersaline wastewater such as the produced water from the oil and gas industry, which has salinities of up to greater than 300,000 mg/L of total dissolved solid (TDS) (Chang et al., 2019).

However, the applications of MD desalination are challenged by the pervasive issue of membrane pore wetting (Boo et al., 2016). In MD, the transport of water vapor across a hydrophobic membrane is driven by a partial vapor pressure difference between the hot feedwater and the cold permeate. Pore wetting takes place when the saline feedwater permeates through the membrane pores, contaminating the treated water product. There is a prevalent belief that pore wetting occurs when the

transmembrane pressure exceeds the liquid entry pressure (LEP) of membrane pores, which is determined by the membrane surface chemistry, pore structure, and surface tension of feedwater (Rezaei et al., 2018; Wang et al., 2018). Membrane wetting experiments have been commonly performed to evaluate the robustness (e.g., wetting resistance) of MD process or novel MD membranes, in which surfactants are typically added to the feedwater in a stepwise manner to induce membrane wetting (Wang and Lin, 2017; Rezaei et al., 2017; Huang et al., 2017). The presence of surfactants in MD can simultaneously reduce the surface tension of feedwater and cause active adsorption of surfactant molecules on the surface of membrane pores, resulting in an occurrence of progressive surfactant-induced wetting (Rezaei et al., 2018; Wang et al., 2018; Wang et al., 2019). The critical surface tension and/or surfactant concentration at which membrane pore wetting occurs have been used to assess the wetting resistance of newly developed membranes or to test the viability of MD for the treatment of hypersaline wastewater (Wang and Lin, 2017; Rezaei et al., 2017; Huang et al., 2017; Eykens et al., 2017; Rezaei and Samhaber, 2016). Furthermore, the contact angles of liquids with different surface tensions (e.g.,

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surfactant-laden feedwaters) are also widely employed to evaluate the wetting properties of the membranes and infer their wetting resistance (Liao et al., 2021; Chen et al., 2017).

Surfactants are amphiphilic molecules with a long hydrophobic tail and a hydrophilic head group (Moo-Young, 2011). The head group of a surfactant molecule can carry a positive, negative, or neutral charge (Moo-Young, 2011), with the corresponding surfactants being classified as cationic, anionic, and non-ionic surfactants, respectively. The chain length of hydrophobic tail and charge of the head group affect the behavior of surfactants in aqueous environments. A longer hydrocarbon chain relates to a higher molecular weight and decreased solubility (Farn, 2006). Also, the Stokes–Einstein equation establishes an inverse relationship between molecular size and diffusion coefficient of the surfactant (Anon). Hence, a larger surfactant generally has a smaller diffusion coefficient and less mobility (Liao et al., 2021; Chen et al., 2017). In the case of MD, the diffusion of surfactants has been found to influence wetting kinetics due to their different rates of transport to the membrane surface (Wang et al., 2019). Additionally, the head charges affect the fate and transport of surfactants in aqueous environments. In natural waters, it has been found that electrostatic interactions affect the adsorption of surfactants to particulate matter and minerals (Farn, 2006, Anon). Cationic surfactants have been found to have the highest adsorption rate due to its electrostatic attraction to soil particles (Ying, 2006).

Although the wetting behavior of MD membrane is potentially linked to surfactant properties, an explicit correlation between wetting behavior and surfactant properties has yet to be established. In recent years, several studies have aimed to delve into understanding the mechanisms of surfactant-induced wetting in MD (Wang et al., 2018; Wang et al., 2019; Hou et al., 2020; Wang et al., 2018). Specifically, attention has been directed towards assessing how varying the hydrophobicity of surfactants influences the wetting behavior. The prevailing consensus suggests that surfactants with a lower hydrophilic-lipophilic balance (HLB), or greater hydrophobic characteristics, tend to be more readily adsorbed onto the membrane surface, thereby enhancing pore wetting (Hou et al., 2020; Wang et al., 2018). However, it remains unclear how surfactants varying in other properties such as size and charge might lead to differences in wetting behaviors in MD for feedwaters of similar surface tensions. As a result, it is imperative to design experiments that reasonably correlate the structure and properties of surfactants with their capabilities of inducing pore wetting.

In this study, we conduct a comparative analysis of the wetting behaviors of various surfactants with different charges and molecular weights in MD desalination. Our approach involves both contact angle measurements and wetting potential characterization through direct contact membrane distillation (DCMD) experiments. Multiple concentrations of each surfactant were used to examine the changes in the wetting potential as function of surfactant type for a hydrophobic polyvinylidene fluoride (PVDF) membrane. The induction time of surfactants to initiate pore wetting was correlated to contact angle and surface tension of the feedwater. Our results demonstrate that different surfactants resulting in similar surface tensions can lead to drastically different wetting potential, suggesting that both charge of head group and molecular weight of surfactants have significant influence on membrane pore wetting. Further, while contact angles generally correlate with the wetting potential of feed solution, higher contact angles of surfactant-containing feedwater do not necessarily lead to longer induction time. We envision that these results are not only paving the way for improving our fundamental understanding of surfactant-induced wetting, but also important for assessing wetting behaviors and membrane wetting resistance for MD desalination.

2. Materials and methods

2.1. Materials and chemicals

The MD membranes used in this study were commercial PVDF Durapore membranes (HVHP, Merck Millipore) with a nominal pore size of 0.45 μm . For all the experiments conducted in this work, commercial PVDF membranes of the same batch were used and expected to have very similar (if not the same) pore size distribution, which was characterized in our prior work (Wang et al., 2019). Sodium chloride (NaCl) and Tween 20 were acquired from Fisher Scientific and used as received. The other surfactants, including sodium dodecyl sulfate (SDS, 99%), Triton X-100, hexadecyltrimethylammonium bromide (CTAB, 99%), dodecyltrimethylammonium bromide (DTAB, 99%), were purchased from Sigma-Aldrich and used as received.

2.2. Surface tension and contact angle measurements

The dynamic surface tensions of 1 M NaCl solutions containing surfactants at different concentrations were measured using the inverted pendant bubble method. In a typical measurement, a quartz cell filled with the solution was placed in an environmental chamber, which was mounted on the leveling stage of a contact angle goniometer (Rame-Hart 260). An inverted stainless steel needle attached to a micro-syringe was submerged into the solution. The environmental chamber was then heated using a temperature controller. When the temperature of the solution reached 60 $^{\circ}\text{C}$ (i.e., the operating temperature of MD experiments), an air bubble attached to the needle tip was created using the micro-syringe. The dynamic surface tension of the solution was determined by analyzing the time evolution of bubble shape.

The apparent contact angles of all solutions on the porous PVDF membranes at 60 $^{\circ}\text{C}$ were characterized in the environmental chamber using the contact angle goniometer. In a typical measurement, the PVDF membrane was placed in the environmental chamber, which was then heated until the surface temperature of the membrane reached 60 $^{\circ}\text{C}$. Subsequently, a solution droplet with a volume of 8 μL (the solution was pre-heated to 60 $^{\circ}\text{C}$ in an oven) was placed on the membrane surface. The apparent contact angle was measured within 10 s after placing the droplet on the surface. For each solution, three contact angle measurements were conducted. Furthermore, the apparent contact angles of surfactant solutions on the PVDF membrane at room temperature ($\sim 20^{\circ}\text{C}$) were also measured.

2.3. MD wetting experiments

A custom-built, crossflow DCMD system equipped with the hydrophobic PVDF membrane was used to treat surfactant-containing saline feed solutions. The membrane flow cell has a dimension of 77 mm \times 26 mm \times 3 mm, with an effective membrane area of 20.02 cm^2 . The volume of the feed solution was 1000 mL, and the temperatures of the feed and permeate streams were maintained at 60 $^{\circ}\text{C}$ and 20 $^{\circ}\text{C}$, respectively. For each experiment, 1 M NaCl solution was used as the feed solution, and deionized water was used as the distillate. For each surfactant used, multiple concentrations that correspond to different surface tensions were used. The crossflow velocities were 9.6 cm s^{-1} and 6.4 cm s^{-1} for the feed and permeate streams, respectively. The real-time water vapor flux and salt rejection rate were calculated based on the changes in weight and conductivity of the permeate reservoir. These values were measured using a top-loading digital balance (Cole-Parmer) and a bench-top conductivity meter (Oakton Instrument), respectively.

Before the addition of surfactant, the DCMD system was operated for 30 min to establish a consistent baseline flux. Next, the surfactant was added to the feed solution to reduce the surface tension of the feed solution in a stepwise manner. During the experiments, the mass and conductivity of the permeate were recorded every minute to calculate the water vapor flux and salt rejection rate. In these experiments, an

induction time of pore wetting was defined as the time when the salt rejection dropped below 95%. For each surfactant concentration, the experiments were replicated three times, using a fresh membrane for each experiment.

3. Results and discussion

3.1. Surface tension and contact angle

The equilibrium surface tensions of 1 M NaCl solutions containing different surfactant at 60 °C (the operational temperature of MD) were measured using the inverted pendant bubble method (see Materials and methods section). Five different surfactants were used in the current study (Fig. 1A), which have either the same carbon chain length but head groups of different charges (e.g., SDS vs. DTAB) or the same charge but different chain lengths (e.g., DTAB vs. CTAB). The shape of an air bubble formed in the surfactant solution was analyzed to determine the surface tension γ_{lv} . When a new liquid-air interface is formed in a surfactant solution, the adsorption of surfactant molecules at the interface leads to the reduction of interfacial tension. The adsorption kinetics of the surfactant is affected by both the surfactant properties (i.e., molecular structure and charge type) and the liquid properties, which is a time-dependent process until the equilibrium interfacial tension is reached. Therefore, temporal evolution of the liquid-air interfacial tension (i.e., dynamic surface tension) was characterized, and the plateau value was used as the equilibrium surface tension (Figure S1, Supplementary Materials). For all surfactant solutions, the surface tension decreased rapidly with increasing the surfactant concentration (Fig. 1B). The temporal evolution of surface tension indicates that the equilibration time (i.e., the time required to reach the equilibrium surface tension) decreased with increasing the surfactant concentration (Figure S1), which was due to increased adsorption rate of surfactant molecules at the interface as the bulk surfactant concentration increases (Atkin et al., 2000; Atkin et al., 2003; Daniel and Berg, 2003). The time scale for attaining equilibrium surface tension can vary significantly for

different surfactants due to different adsorption kinetics, which is affected by the surfactant properties as well as the surfactant-electrolyte (NaCl) interaction (Atkin et al., 2003; Atkin et al., 2000; Diamant et al., 2001; Qazi et al., 2020). Prior work has demonstrated that the adsorption of surfactant at the interfaces affects the kinetics of membrane pore wetting in MD process (Wang et al., 2018). Although not quantified in this study, the varied adsorption kinetics of different surfactants at the interfaces and the associated surfactant transport, which have been studied extensively in prior work, can potentially significantly affect the pore-wetting process in MD (Atkin et al., 2000; Diamant et al., 2001; Zhang et al., 2007; Diamant and Andelman, 1996). Therefore, surfactants exhibiting different adsorption kinetics may lead to distinct pore wetting behaviors and consequently different induction times.

We further measured the apparent contact angles of surfactant solutions at 60 °C on PVDF membranes. For all surfactant solutions, the apparent contact angle decreased with decreasing surface tension (i.e., increasing surfactant concentration) (Fig. 1C). However, at very similar surface tensions, the surfactant solutions exhibited different wetting behaviors, which were signified by the variation of apparent contact angle. For example, the surface tensions of 0.06 mM SDS, 0.4 mM DTAB, and 0.005 mM CTAB are 50.1 mN/m, 51.1 mN/m, and 50.5 mN/m, respectively. However, their apparent contact angles on the membrane surface were $109^\circ \pm 2^\circ$, $105^\circ \pm 2^\circ$, and $115^\circ \pm 3^\circ$, respectively (statistical analysis confirms a significant difference in comparing apparent contact angles between SDS and DTAB solutions, between SDS and CTAB solutions, and between CTAB and DTAB solutions, with the *p*-values at 0.071, 0.009, and 0.045, respectively). Furthermore, some surfactant solutions with lower surface tensions displayed higher apparent contact angles than other surfactant solutions with higher surface tensions. For example, the contact angle of 0.04 mM Tween 20 with γ_{lv} of ~ 33 mN/m was $\sim 110^\circ$, which was higher than that ($\sim 106^\circ$) of 0.03 mM Triton X-100 with γ_{lv} of ~ 41.3 mN/m. These results are due to the fact that the interactions (e.g., hydrophobic and electrostatic interactions) between surfactant and solid surface as well as the surfactant properties (e.g., chain length and charge type) have significant influence on the packing

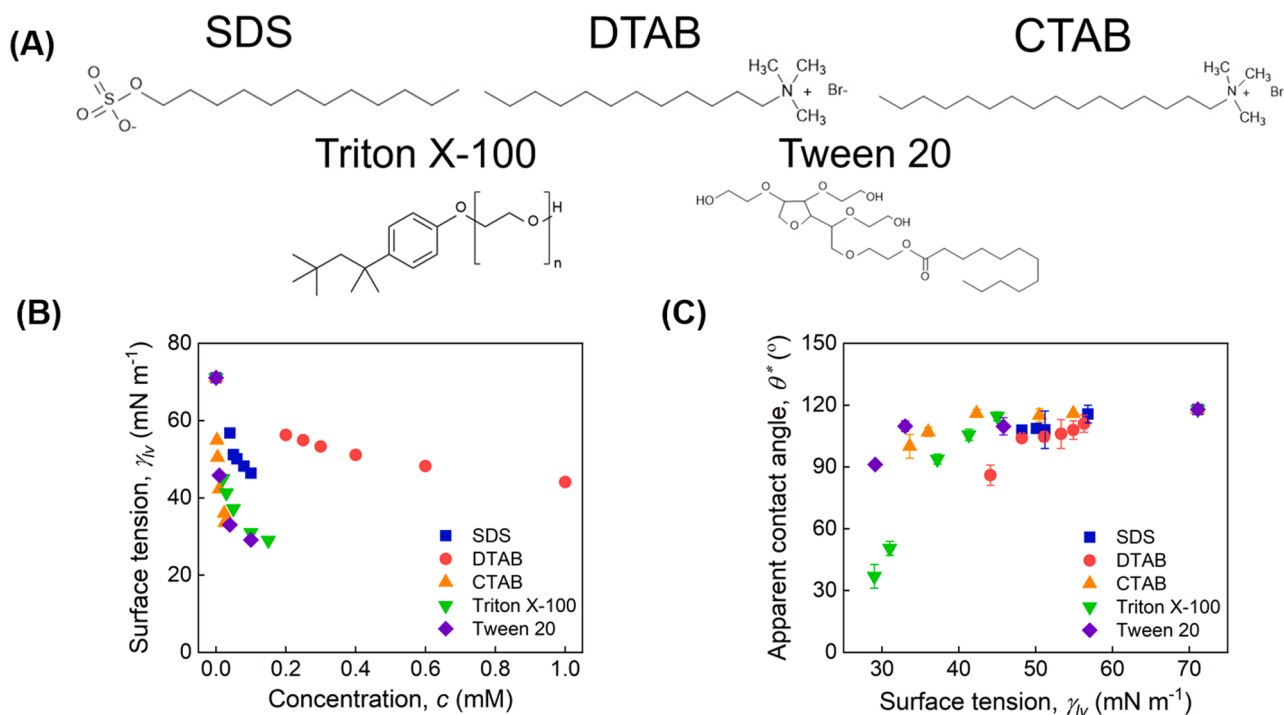


Fig. 1. (A) Molecular structures of the five surfactants. (B) Surface tensions of 1 M NaCl solutions containing surfactants of different concentrations at 60 °C. (C) The apparent static contact angles of surfactant solutions with different surface tensions on the PVDF membranes at 60 °C. The error bars represent the standard deviation calculated from three independent measurements.

of the surfactant molecules at the liquid-solid interface, which could alter the solid surface energy and consequently affects the wetting behavior of the surfactant solutions (Abdel-Rahem, 2008; Mohammadi et al., 2004).

3.2. The effects of surfactant property on induction time of membrane wetting

To explore the relationship between surfactant property and capability of inducing pore wetting, we investigated the wetting behaviors of dynamic, crossflow MD experiments in the presence of different surfactants. All the surfactants were able to cause membrane wetting in MD (Figure S2, Supplementary Materials), with membrane wetting (indicated by a decrease of salt rejection accompanied by an increase of water vapor flux) occurring earlier at a higher surfactant concentration (corresponding to a lower surface tension of feedwater). We observed that pore wetting induced by these surfactants was transient (which was clearer for relatively low surfactant concentrations) rather than instantaneous. Such an observation is consistent with the findings of Wang et al. (2018, 2018), who described surfactant-induced wetting as combined processes of adsorption-driven depletion and transport-driven replenishment. To compare the wetting capabilities of surfactants fairly, we determined the induction time of each surfactant at different concentrations and correlated it with the feedwater surface tension (Fig. 2).

As shown in Fig. 2A, SDS demonstrated a longer induction time than DTAB at comparable feedwater surface tensions, despite their same lengths of the carbon chain. For example, the induction time of SDS at a feedwater surface tension of ~ 51 mN/m was ~ 77 min, which was much longer than that of DTAB at a very similar feedwater surface tension (~ 51 mN/m, ~ 12 min). This result indicates that positively charged DTAB led to a faster rate of pore wetting than negatively charged SDS. Such a difference in the kinetics of pore wetting between SDS and DTAB can be explained by their electrostatic interactions with the membrane surface. We note that electrostatic interactions are weakened under high-salinity conditions. However, Li et al. demonstrated that in a variety of high salinity brines an anionic polyelectrolyte successfully removed cationic pollutants through electrostatic attraction, indicating that electrostatic interaction can still exist in highly saline brines (Li et al., 2024). Indeed, debates still exist regarding the mechanism of pore wetting induced by surfactants. The autophilic effect, which assumes that the adsorption of surfactants on the hydrophobic surface reverses surface wettability to hydrophilic, has been used to explain membrane wetting in MD (Horseman et al., 2021; Chang et al., 2023; Nthunya et al., 2024). According to this theory, the electrostatic attraction between DTAB and the negatively charged PVDF membrane (Boo et al., 2016) results in easier adsorption of DTAB onto the membrane surface and consequently a faster pore wetting, whereas the adsorption of SDS is retarded due to its electrostatic repulsion by the PVDF membrane

surface (Fig. 3A). However, Wang et al. suggests that the transport of surfactants to the wetting frontier by advective transport and diffusion is the key to inducing pore wetting during MD desalination (Wang et al., 2018; Wang et al., 2019; Wang et al., 2018). According to this theory, the electrostatic repulsion between the PVDF membrane and SDS hinders the transport of SDS towards and inside the membrane pores, thereby slowing the reduction of surface tension for solution near the wetting frontier and the consequent migration of the liquid–air interface towards the distillate.

Fig. 2B compares the induction time of DTAB and CTAB, both of which are positively charged but have different molecular weights. Compared to CTAB, DTAB has a smaller molecular weight and a shorter carbon tail, demonstrating lower induction time and a higher capability of inducing pore wetting. The results for non-ionic surfactants mirrored those for cationic surfactants, where Tween 20 with a smaller molecular weight displayed a shorter induction time to initiate membrane wetting than Triton X-100 (Fig. 2C). The variations in wetting behavior between surfactants with the same type of charge were probably driven by the difference in the rate of molecular diffusion, which determines the time required to reduce the feedwater surface tension at the wetting frontier (Ying, 2006; Alves et al., 2020). The surfactants of higher molecular weights (CTAB and Triton X-100 in this study) possess smaller diffusion coefficients, and thus a smaller number of surfactants are able to transport to the wetting frontier within the same timeframe (Fig. 3B), leading to longer induction times when sufficient surfactants are accumulated to lower the feedwater surface tension below a certain threshold.

Further, the results of this study contradict the belief that surfactants with a lower HLB, or greater hydrophobic characteristics, tend to be more capable of inducing wetting (Hou et al., 2020; Wang et al., 2018). As such a statement was obtained using a single molar concentration with highly variable surface tensions (Hou et al., 2020; Wang et al., 2018), its validity needs to be revisited. In the current study, the cationic and non-ionic surfactants with higher HLB (i.e., DTAB and Tween 20) indeed exhibited higher wetting capabilities (Table S1, Figs. 2B and 2C). Our results are consistent with a recent publication where surfactants with higher HLB values were more likely to induce membrane wetting (Liao et al., 2021). The authors explain that the weaker hydrophobic-hydrophobic affinity between surfactant and membrane allows surfactants with higher HLB (and correspondingly lower hydrophobicity) to stay in the feed solution in free states, as opposed to absorbing into the membrane pore wall, thereby reducing feed solution's surface tension and membrane LEP more effectively (Liao et al., 2021). Additionally, the membrane surfaces attached by surfactants of higher HLB are more hydrophilic, aiding in the formation of hydrophilic channels and further promoting wetting (Liao et al., 2021). Our results demonstrate that when surfactants with varying properties are tested at comparable surface tensions, higher hydrophobicity of surfactants does not necessarily enhance the wetting potential. Instead, molecular

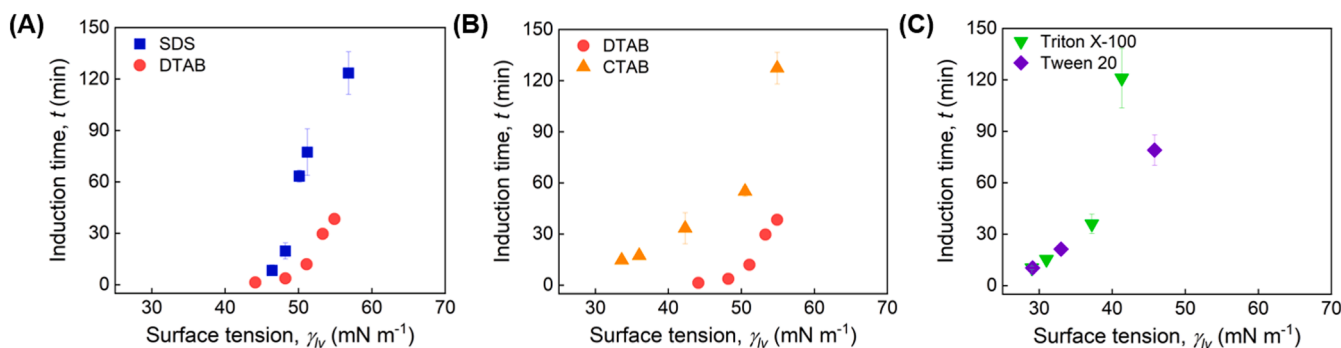


Fig. 2. The induction time of membrane wetting in MD for (A) surfactants of the same carbon chain length but different charge types (SDS vs. DTAB, B) positively charged surfactants of different chain lengths (DTAB vs. CTAB), and (C) non-ionic surfactants of different molecular structures and weights (Tween 20 vs. Triton X-100). The error bars represent the standard deviation calculated from at least three independent tests.

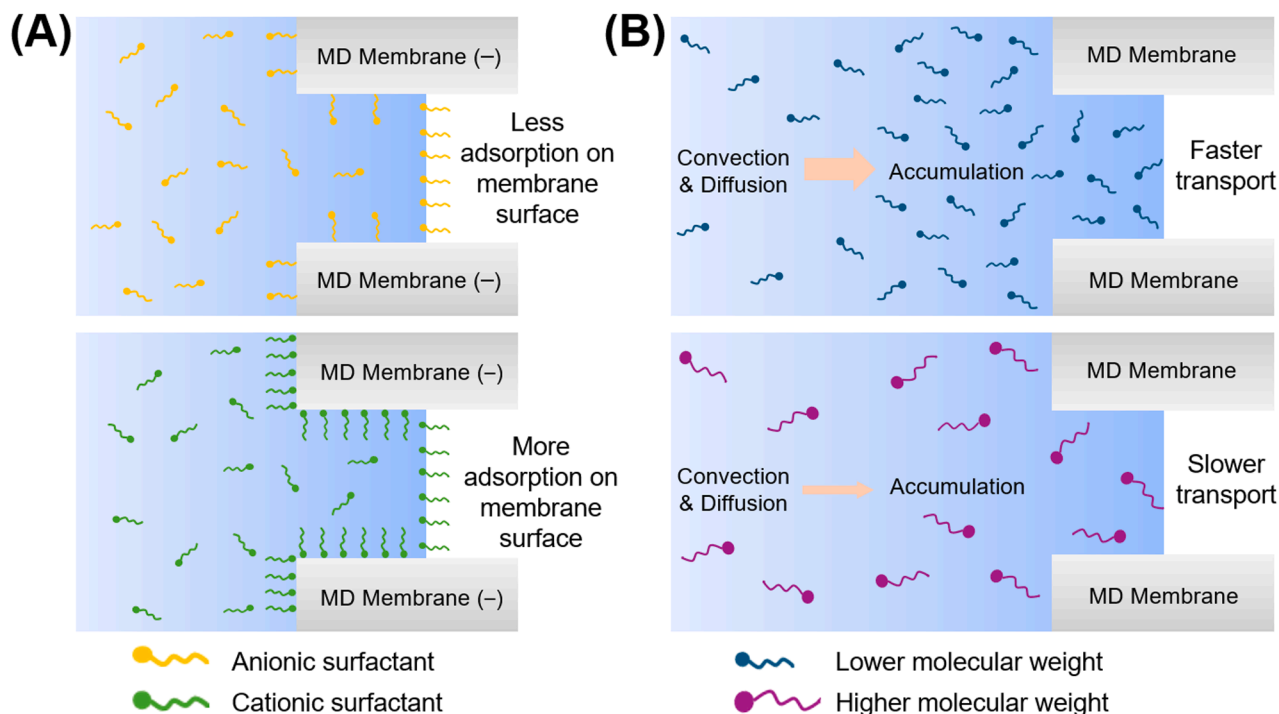


Fig. 3. Schematic illustration of the effects of surfactant-membrane interactions on MD wetting behavior when comparing (A) anionic and cationic surfactants and (B) surfactants with different molecular weights. It is worth mentioning that adsorption and transport (due to convection and diffusion) of surfactants occur at the same time. Thus, separating those two mechanisms of surfactant-membrane interactions is just for simplicity of figure presentation.

properties such as size and charge should be considered when evaluating the wetting potential of surfactant-containing solutions.

In addition, we explored the relationship between the induction time of pore wetting and the apparent contact angles measured at both room temperature and 60 °C for the same surfactant solutions. As shown in Fig. 4, although a higher apparent contact angle generally led to longer induction time, the induction time could vary significantly for the same (or very similar) contact angle. For example, when the apparent contact angle at room temperature was $\sim 120^\circ$, the induction time of pore wetting varied between ~ 120 min and <20 min (Fig. 4A). A similar phenomenon was observed when the apparent contact angles at 60 °C were used (e.g., when the apparent contact angle was $\sim 110^\circ$, Fig. 4B). These results suggest that the apparent contact angle of aqueous solutions containing surfactants on the membrane surface (regardless of the temperature at which the contact angle is measured), which has been

widely used to indicate solution wetting potential, is an unreliable measure for assessing the solution wetting potential for MD process (Wang and Lin, 2017; Ismail et al., 2022; Gekas et al., 1992; Kung et al., 2019; Huhtamäki et al., 2018). Indeed, according to the results of our study, it is unlikely that a single descriptor can accurately forecast membrane pore wetting caused by surfactants under MD conditions due to the multifaceted nature of the problem. We anticipate that multi-parameter modeling, which considers various surfactant and membrane properties, is a potentially feasible approach for establishing a predictive model for forecasting pore wetting caused by surfactants.

4. Conclusion

In this study, we performed a systematic study to investigate and compare the wetting behaviors of various surfactants with different

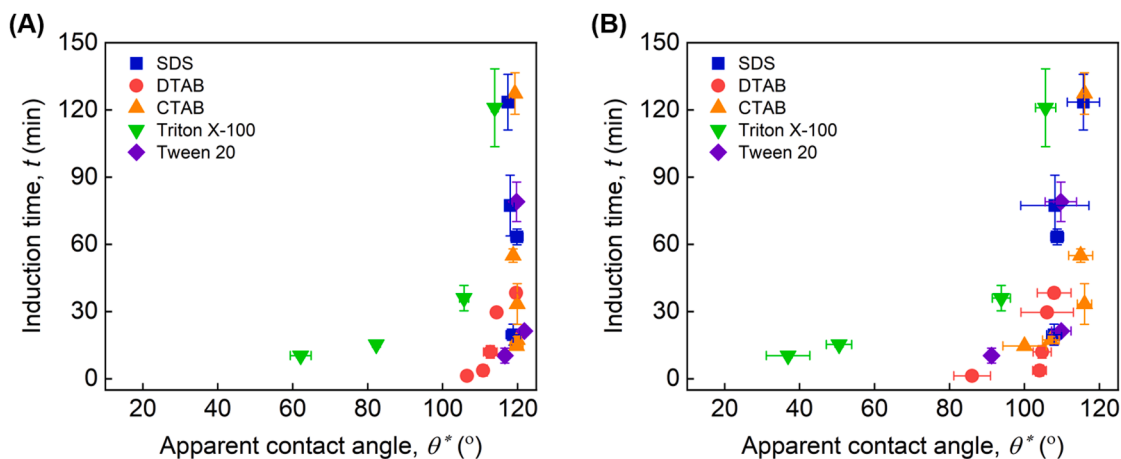


Fig. 4. The induction time of membrane wetting as a function of apparent contact angle of the surfactant solution measured at (A) room temperature ($\sim 20^\circ\text{C}$) and (B) 60°C . The error bars represent the standard deviation calculated from three independent measurements.

charges and molecular weights in MD desalination. Several previous studies have compared surfactants at a single molar concentration, thereby neglecting the unique surface tension-concentration relationship of each surfactant. As wastewater generated from different sources may have highly variable surfactant constituents and surface tensions, applying a sole surfactant at a singular concentration is not sufficient to evaluate the capability of surfactants to induce pore wetting in MD desalination. When surfactants at similar surface tensions are compared, we discovered that surfactant properties such as charge and molecular weight play an important role in regulating the wetting behavior. Especially, when comparing surfactants of similar size but differing charges, cationic surfactants exhibited a higher wetting capability likely due to electrostatic attraction between surfactant molecules and membrane surface. When comparing surfactants of similar charges, surfactants with larger molecular sizes exhibited a lower wetting potential, because of slower rates of surfactant transport to the membrane surface.

Furthermore, our results demonstrate that parameters that have been commonly used to indicate wetting potential, including apparent contact angle and solution surface tension, are not reliable to predict wetting behavior of MD, which is intricately linked with surfactant properties such as charge and molecular size. As a result, the wetting behavior of MD is likely different from those revealed in studies where a single type of surfactant is used. We suggest that it is necessary to use surfactant-containing feed solutions with not only varying surface tensions but also different types of surfactants to comprehensively understand the wetting behavior of MD desalination and evaluate the wetting resistance of newly developed membrane materials. In the future research, a comprehensive investigation, which involves liquid spreading and imbibition kinetics, is perhaps needed to further understand the influence and significance of surfactants in regulating membrane pore wetting in MD. Additionally, membrane properties, such as pore size distribution, charge, and hydrophobicity, can significantly affect pore wetting. Performing the experimental protocol with altered membrane properties could affect the membrane-surfactant interactions and dictate the liquid's propensity to penetrate the membrane pores. Although this study's purpose is to convey the ideas that surfactant-induced pore wetting in MD processes is complex and that the conventional criteria used to assess the wetting potential are not reliable for MD membranes, expanding the experimental protocol to evaluate the effects of membrane properties is an avenue for future work that could provide more insight into predicting the wetting capabilities of surfactant-laden solutions.

CRediT authorship contribution statement

Connor Coolidge: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Azal Mohammed Hassan Alhadidi:** Formal analysis, Data curation. **Wei Wang:** Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Tiezheng Tong:** Writing – review & editing, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Tiezheng Tong reports financial support was provided by National Science Foundation. Wei Wang reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.memlet.2024.100077](https://doi.org/10.1016/j.memlet.2024.100077).

References

- Atkin, R., 1924. The Stokes-Einstein law for diffusion in solution. *Proceedings of the Royal Society London A* 106, 724–749. <https://doi.org/10.1098/rspa.1924.0100>.
- Abdel-Rahem, R., 2008. The influence of hydrophobic counterions on micellar growth of ionic surfactants. *Adv. Colloid. Interface Sci.* 141, 24–36. <https://doi.org/10.1016/j.cis.2008.02.002>.
- Alves, A.V., Tsianou, M., Alexandridis, P., 2020. Fluorinated surfactant adsorption on mineral surfaces: implications for PFAS fate and transport in the environment. *Surfaces* 3, 516–566. <https://doi.org/10.3390/surfaces3040037>.
- Atkin, R., Craig, V.S.J., Biggs, S., 2000. Adsorption kinetics and structural arrangements of cationic surfactants on silica surfaces. *Langmuir* 16, 9374–9380. <https://doi.org/10.1021/la0001272>.
- Atkin, R., Craig, V.S.J., Wanless, E.J., Biggs, S., 2003. Mechanism of cationic surfactant adsorption at the solid–aqueous interface. *Adv. Colloid. Interface Sci.* 103, 219–304. [https://doi.org/10.1016/S0001-8686\(03\)00002-2](https://doi.org/10.1016/S0001-8686(03)00002-2).
- Boo, C., Lee, J., Elimelech, M., 2016. Omniphobic polyvinylidene fluoride (pvdf) membrane for desalination of shale gas produced water by membrane distillation. *Environ. Sci. Technol.* 50, 12275–12282. <https://doi.org/10.1021/acs.est.6b03882>.
- Chang, H., Li, T., Liu, B., Vidic, R.D., Elimelech, M., Crittenden, J.C., 2019. Potential and implemented membrane-based technologies for the treatment and reuse of flowback and produced water from shale gas and oil plays: a review. *Desalination* 455, 34–57. <https://doi.org/10.1016/j.desal.2019.01.001>.
- Chang, H., Zhu, Y., Huang, L., Yan, Z., Qu, F., Liang, H., 2023. Mineral scaling induced membrane wetting in membrane distillation for water treatment: fundamental mechanism and mitigation strategies. *Water Res.* 247, 120807. <https://doi.org/10.1016/j.watres.2023.120807>.
- Chen, Y., Tian, M., Li, X., Wang, Y., An, A.K., Fang, J., He, T., 2017. Anti-wetting behavior of negatively charged superhydrophobic PVDF membranes in direct contact membrane distillation of emulsified wastewaters. *J. Memb. Sci.* 535, 230–238. <https://doi.org/10.1016/j.memsci.2017.04.040>.
- Daniel, R.C., Berg, J.C., 2003. A simplified method for predicting the dynamic surface tension of concentrated surfactant solutions. *J. Colloid. Interface Sci.* 260, 244–249. [https://doi.org/10.1016/S0021-9797\(02\)00148-0](https://doi.org/10.1016/S0021-9797(02)00148-0).
- Deshmukh, A., Boo, C., Karanikola, V., Lin, S., Straub, A.P., Tong, T., Warsinger, D.M., Elimelech, M., 2018. Membrane distillation at the water–energy nexus: limits, opportunities, and challenges. *Energy Environ. Sci.* 11, 1177–1196. <https://doi.org/10.1039/C8EE00291F>.
- Diamant, H., Andelman, D., 1996. Kinetics of surfactant adsorption at fluid–fluid interfaces. *J. Phys. Chem.* 100, 13732–13742. <https://doi.org/10.1021/jp960377k>.
- Diamant, H., Ariel, G., Andelman, D., 2001. Kinetics of surfactant adsorption: the free energy approach. *Colloids Surf. A* 183–185, 259–276. [https://doi.org/10.1016/S0927-7757\(01\)00553-2](https://doi.org/10.1016/S0927-7757(01)00553-2).
- Eykens, L., De Sitter, K., Dotremont, C., De Schepper, W., Pinoy, L., Van Der Bruggen, B., 2017. Wetting resistance of commercial membrane distillation membranes in waste streams containing surfactants and oil. *Appl. Sci.* 7, 118. <https://doi.org/10.3390/app7020118>.
- Farn, R.J. (Ed.), 2006. *Chemistry and Technology of Surfactants*. Blackwell Pub, Oxford; Ames, Iowa.
- Gekas, V., Persson, K.M., Wahlgren, M., Sivik, B., 1992. Contact angles of ultrafiltration membranes and their possible correlation to membrane performance. *J. Memb. Sci.* 72, 293–302. [https://doi.org/10.1016/0376-7388\(92\)85056-O](https://doi.org/10.1016/0376-7388(92)85056-O).
- Horseman, T., Yin, Y., Christie, K.S., Wang, Z., Tong, T., Lin, S., 2021. Wetting, scaling, and fouling in membrane distillation: state-of-the-art insights on fundamental mechanisms and mitigation strategies. *ACS EST Eng.* 1, 117–140. <https://doi.org/10.1021/acsestengg.0c00025>.
- Hou, D., Yuan, Z., Tang, M., Wang, K., Wang, J., 2020. Effect and mechanism of an anionic surfactant on membrane performance during direct contact membrane distillation. *J. Memb. Sci.* 595, 117495. <https://doi.org/10.1016/j.memsci.2019.117495>.
- Huang, Y.-X., Wang, Z., Jin, J., Lin, S., 2017. Novel janus membrane for membrane distillation with simultaneous fouling and wetting resistance. *Environ. Sci. Technol.* 51, 13304–13310. <https://doi.org/10.1021/acs.est.7b02848>.
- Huhtamäki, T., Tian, X., Korhonen, J.T., Ras, R.H.A., 2018. Surface-wetting characterization using contact-angle measurements. *Nat. Protocol* 13, 1521–1538. <https://doi.org/10.1038/s41596-018-0003-z>.

- Ismail, M.F., Islam, M.A., Khorshidi, B., Tehrani-Bagha, A., Sadrzadeh, M., 2022. Surface characterization of thin-film composite membranes using contact angle technique: review of quantification strategies and applications. *Adv. Colloid Interface Sci.* 299, 102524 <https://doi.org/10.1016/j.cis.2021.102524>.
- Kung, C.H., Sow, P.K., Zahiri, B., Mérida, W., 2019. Assessment and interpretation of surface wettability based on sessile droplet contact angle measurement: challenges and opportunities. *Adv. Mater. Interfaces* 6, 1900839. <https://doi.org/10.1002/admi.201900839>.
- Li, C., Wang, H., Xu, X., Liu, M., Liu, Y., He, S., Qian, Y., Li, Z., 2024. Anionic polyelectrolyte modified perovskite composite activated hydrogen peroxide to treat high-salinity organic wastewater: dual effects of electrostatic interaction. *Chem. Eng. J.* 488, 151033 <https://doi.org/10.1016/j.cej.2024.151033>.
- Liao, X., Wang, Y., Liao, Y., You, X., Yao, L., Razaqpur, A.G., 2021. Effects of different surfactant properties on anti-wetting behaviours of an omniphobic membrane in membrane distillation. *J. Memb. Sci.* 634, 119433 <https://doi.org/10.1016/j.memsci.2021.119433>.
- Mohammadi, R., Wassink, J., Amirfazli, A., 2004. Effect of surfactants on wetting of super-hydrophobic surfaces. *Langmuir* 20, 9657–9662. <https://doi.org/10.1021/la049268k>.
- Moo-Young, M., 2011. *Comprehensive Biotechnology*, 2nd ed. Elsevier, Amsterdam.
- Nthunya, L.N., Pinier, J., Ali, A., Quist-Jensen, C., Richards, H., 2024. Valorization of acid mine drainage into potable water and valuable minerals through membrane distillation crystallization. *Sep. Purif. Technol.* 334, 126084 <https://doi.org/10.1016/j.seppur.2023.126084>.
- Qazi, M.J., Schlegel, S.J., Backus, E.H.G., Bonn, M., Bonn, D., Shahidzadeh, N., 2020. Dynamic surface tension of surfactants in the presence of high salt concentrations. *Langmuir* 36, 7956–7964. <https://doi.org/10.1021/acs.langmuir.0c01211>.
- Rezaei, M., Warsinger, D.M., Lienhard V, J.H., Duke, M.C., Matsuura, T., Samhaber, W.M., 2018. Wetting phenomena in membrane distillation: mechanisms, reversal, and prevention. *Water Res.* 139, 329–352. <https://doi.org/10.1016/j.watres.2018.03.058>.
- Rezaei, M., Warsinger, D.M., Lienhard V, J.H., Samhaber, W.M., 2017. Wetting prevention in membrane distillation through superhydrophobicity and recharging an air layer on the membrane surface. *J. Memb. Sci.* 530, 42–52. <https://doi.org/10.1016/j.memsci.2017.02.013>.
- Rezaei, Mohammad, Samhaber, Wolfgang, 2016. Wetting behaviour of superhydrophobic membranes coated with nanoparticles in membrane distillation. *Chem. Eng. Trans.* 47, 373–378. <https://doi.org/10.3303/CET1647063>.
- Wang, W., Du, X., Vahabi, H., Zhao, S., Yin, Y., Kota, A.K., Tong, T., 2019b. Trade-off in membrane distillation with monolithic omniphobic membranes. *Nat. Commun.* 10, 3220. <https://doi.org/10.1038/s41467-019-11209-6>.
- Wang, Z., Chen, Y., Lin, S., 2018b. Kinetic model for surfactant-induced pore wetting in membrane distillation. *J. Memb. Sci.* 564, 275–288. <https://doi.org/10.1016/j.memsci.2018.07.010>.
- Wang, Z., Chen, Y., Sun, X., Duddu, R., Lin, S., 2018a. Mechanism of pore wetting in membrane distillation with alcohol vs. surfactant. *J. Memb. Sci.* 559, 183–195. <https://doi.org/10.1016/j.memsci.2018.04.045>.
- Wang, Z., Chen, Y., Zhang, F., Lin, S., 2019a. Significance of surface excess concentration in the kinetics of surfactant-induced pore wetting in membrane distillation. *Desalination* 450, 46–53. <https://doi.org/10.1016/j.desal.2018.10.024>.
- Wang, Z., Lin, S., 2017. Membrane fouling and wetting in membrane distillation and their mitigation by novel membranes with special wettability. *Water Res.* 112, 38–47. <https://doi.org/10.1016/j.watres.2017.01.022>.
- Ying, G.-G., 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. *Environ. Int.* 32, 417–431. <https://doi.org/10.1016/j.envint.2005.07.004>.
- Zhang, X., Chen, B., Wang, Z., 2007. Computer simulation of adsorption kinetics of surfactants on solid surfaces. *J. Colloid. Interface Sci.* 313, 414–422. <https://doi.org/10.1016/j.jcis.2007.05.003>.