Significance of Surface Excess Concentration in the Kinetics of Surfactant-induced Pore Wetting in Membrane Distillation

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ABSTRACT

Failure of membrane distillation (MD) due to pore wetting by amphiphilic molecules has recently received growing interests because it is a critical challenge to overcome for MD to be applicable for treating unconventional feed water. Recent MD studies using feed solutions containing surfactants have elucidated fundamental mechanism of wetting and generated practical solutions for wetting mitigation. However, what remains unclear is the impact of surfactant species on pore wetting kinetics. Based on a recently developed kinetic model for surfactant-induced pore wetting in MD, we hypothesize that the surface excess concentration of a surfactant is the most important surfactant property in affecting the pore wetting kinetics. In this study, we performed controlled MD wetting experiments using seven different types of surfactants and measured their respective breakthrough time as a quantitative metric for wetting kinetics. Our experiments reveal a good linear correlation between the surface excess concentration and breakthrough time for most but one tested surfactant. When surface excess concentration and diffusion coefficient are both considered, the model-simulated breakthrough time matches the experimentally measurement remarkably well for all tested surfactants.

1. Introduction

Pore wetting is a unique technical challenge in membrane distillation (MD)—a membrane-based thermal distillation technology that has recently attracted extensive interests in research and development due to its promising application in treating hypersaline brine using low-grade thermal energy [1–10]. Pore wetting in MD refers to the penetration of salty feed water through membrane pores, which results in unacceptable salt rejection [11–14]. It can be caused by the presence of low-surface-tension and water miscible liquids (e.g. alcohol) or amphiphilic molecules (e.g. synthetic or natural surfactants) [15–20]. Recently, it has been shown that biofouling in MD can also induce wetting via generation of biological surfactants [21]. Another possible cause of pore wetting is mineral scaling [22,23], even though the exact mechanism remains unclear.

The general principle of pore wetting based on the concept of liquid entry pressure (LEP) has long been proposed [15]. It provides an important guiding principle for developing material or operational strategies to mitigate or prevent pore wetting in MD. However, with amphiphilic molecules that can actively adsorb onto the pore surface, this general principle cannot be directly applied using LEP calculated with the surface tension of the feed solution containing the amphiphilic wetting agents [24]. Neither does this principle alone provide any information regarding the kinetic rate of pore wetting and how it is affected by operating parameters [25].

We recently developed a model to predict the kinetics of pore wetting induced by surfactants [25]. This kinetic model captures the fact that adsorption of surfactants onto the pore surface reduces the aqueous concentration of surfactants and thereby increases the surface tension of the feed solution at the wetting frontier (i.e. the liquid-air interface). Based on this model, the kinetics of wetting is dominantly determined by how fast the pore surface is saturated or "packed" by the adsorbed surfactants, which in turn depends on how fast the surfactants transport from the bulk solution to the wetting frontier. This model was successfully employed to explain several important experimental observations, including the dependence of wetting kinetics on vapor flux, on bulk concentration of surfactants, and on transmembrane pressure.

It has been reported in literature that different types of surfactants have very different wetting behaviors in MD [26,27]. Specifically, different surfactants at the same molar concentration can result in very different wetting kinetics. Such difference in wetting behavior was attributed to the different hydrophilic-lipophilic balance (HLB) which is one of the most important parameters for a surfactant. HLB quantifies to what degree a surfactant is hydrophilic or lipophilic and thus

dictates its partition between water and oil [28]. However, the adsorption of amphiphilic molecules onto a hydrophobic surface is energetically highly favorable due to the strong hydrophobic interaction between the hydrophobic end of the molecule and the hydrophobic surface [29,30], and should thus be controlled by the rate of surfactant transport. In other words, even though strength of the interaction between surfactants and hydrophobic pore surface may vary depending on HLB, it should have negligible impact on the adsorption kinetics, because the adsorption is always limited by transport in the absence of energy barrier. An analogous scenario can be found in colloidal aggregation or deposition, whereas the strength of particle-particle or particle-surface interaction is relevant only if an energy barrier exists [31]. When the energy barrier is eliminated, the aggregation or deposition kinetics become diffusion limited and the strength of attractive interaction is irrelevant due to its very short range. Based on this argument, the kinetics of wetting should have little direct correlation with HLB.

In this study, we investigate the kinetics of membrane pore wetting in direct contact MD (DCMD) process induced by different types of surfactants. We first very briefly review the key features of the recently developed kinetic model on pore wetting and highlight the predictions of this model on the impact of surfactant species. We then perform DCMD experiments to quantify the kinetic rates of pore wetting with different types of surfactants and compare the experimental results with theoretical prediction.

2. Theoretical Considerations

The kinetic model of pore wetting was developed based on three major assumptions. The first assumption is pseudo force equilibrium at the wetting frontier as mathematically described by $LEP' = \Delta P$, where ΔP is the transmembrane pressure. Here, LEP' is not the LEP of the feed solution calculated using the bulk concentration of surfactants, but rather the local LEP of the solution at the wetting frontier where the surfactant concentration is reduced due to continuous adsorption onto the pore surface (Fig. 1). The second assumption is pseudo-equilibrium surfactant adsorption, which suggests that adsorption of surfactants from the solution near the wetting frontier to the pore surface surrounding the wetting frontier is very fast compared to axial transport of surfactant from the bulk solution to the wetting frontier, and therefore equilibrium can be assumed. The third assumption is pseudo-steady state transport of surfactants, which suggests that the forward propagation of the wetting frontier is very slow compared to the transport of the

surfactants to the wetting frontier, so that at any given time point, the surfactant transport can be considered as in a pseudo-steady state with a temporarily static wetting frontier. In other words, the profile of surfactant concentration distribution in the axial direction can be considered as constant in the time scale characteristic of surfactant transport which is much shorter than the time scale of wetting frontier propagation.

The wetting frontier moves forward (toward the distillate side) by a differential distance if and only if that "differential ring" around the frontier is fully saturated with the adsorbed surfactants. This is because once that "differential ring" is saturated, it cannot adsorb any more surfactant from the solution near the frontier. Consequently, the surface tension of the solution near the frontier decreases and force equilibrium is temporarily violated, causing the wetting frontier to move forward. Once the wetting frontier moves to the next "differential ring" with no adsorbed surfactant, force equilibrium is restored until the surface of this fresh "differential ring" is again saturated. We note that while this step-wise description may facilitate understanding of the wetting process, the actual wetting process is continuous.

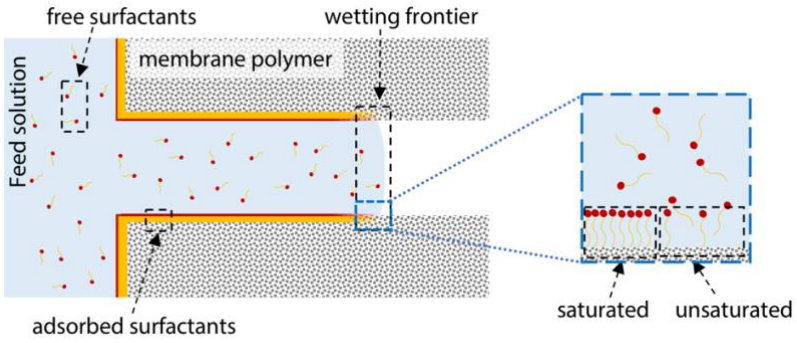

Fig. 1. Schematic of surfactant-induced pore wetting in membrane distillation. The pore surface in contact with the feed solution is in general saturated by the adsorbed surfactants. The only exception is the region that surrounds the wetting frontier which is essentially the "differential plug" of solution near the water-air interface. This region is also referred to as the "differential ring" at the wetting frontier in the following discussion.

With the above model, the kinetics of pore wetting is determined by how fast the pore surface is saturated by adsorbed surfactants because saturation of pore surface is the necessary condition for the forward propagation of wetting frontier. The kinetic rate of pore surface saturation in turn depends on two properties of surfactants. The first property is the (maximum) surface packing

density, τ_{max}, defined as mole of surfactants per area of the saturated pore surface. If τ_{max} is high, it requires a large number of surfactants to fill up a "differential ring". For a given rate of surfactant transport, a system with higher τ_{max} will result in slower wetting.

The second property of surfactants that potentially has an impact on wetting kinetics is the diffusion coefficient. Diffusion coefficient plays an important role in affecting the transport rate of surfactants particularly when the diffusive contribution is significant compared with the convective contribution to the overall surfactant transport. This scenario is rare and only applies when the vapor flux is low or when the concentration gradient of surfactants is significant. However, in most cases to be analyzed in this study, where evaporation-induced convection is the dominant transport mechanism, the diffusion coefficient will have an insignificant impact on pore wetting kinetics.

3. Experimental section

3.1 Materials

The MD membrane utilized in this study was a commercial hydrophobic polyvinylidene fluoride (PVDF) membrane (GE Health Life Sciences, Pittsburgh, PA). The nominal pore size and average thickness of the PVDF membrane are 0.45 and 180 μm, respectively. Sodium chloride (NaCl) and different types of surfactants, including sodium dodecyl sulfate (SDS), sodium dodecyl benzenesulfonate (SDBS), Triton X-100, Cetrimonium bromide (CTAB), Tween 20, Tween 85, and Span 20 were all purchased from Sigma Aldrich and used without further purification.

3.2 Surface tension

The surface tension of NaCl aqueous solutions with different types of surfactants at different concentrations were evaluated by analyzing the shape of reverse pendant drops using an optical tensiometer (TL100, Attention, Finland). Specifically, an air bubble was extruded into the solution using a submerged micro-syringe and stayed attached to the micro-syringe tip. The shape of the air bubble was analyzed using the built-in software of the instrument to obtain the surface tension of the solutions. All measurements were conducted at 60 °C which was the feed temperature for the MD experiments. In almost all cases, the NaCl concentration was maintained at 0.6 M which was the feed concentration in the MD experiments. An additional concentration of 0.3 M was also used for measuring the surface tensions of SDBS for investigating the impact of ionic strength

which also has a strong impact on surface tension. Five measurements were performed for each set of conditions and the mean values were reported with standard deviations.

3.3 Surface excess concentration

The accurate experimental determination of τ_{max} for a given surfactant on PVDF surface, or on any solid surface, is practically rather challenging. However, there is another readily assessible parameters that can be used as a proxy of τ_{max}, which is the surface excess concentration, Γ [32,33]. By definition, Γ is roughly equal to the areal concentration of the surfactants at the air-water interface. Surface excess concentration is numerically similar to τ_{max} for PVDF given that both air and PVDF are sufficiently hydrophobic so that adsorption of surfactants onto the liquid-air interface and the liquid-solid interface is energetically highly favorable in both cases. The accurate estimation of Γ can be readily performed by measuring the surface tension of the solutions with different concentrations of surfactant and applying the Gibbs adsorption equation [34,35]:

$$\Gamma = -\frac{1}{RT}\frac{\partial \gamma}{\partial lnC} \quad (1)$$

where γ is the surface tension of the liquid, C is the molar concentration of the surfactant, R is the ideal gas constant, T is the temperature (333K in our experiments).

3.4 DCMD wetting experiments

Comparative DCMD wetting experiments with different surfactant species were carried out using commercial PVDF membrane with a dimension of 8 cm × 2.5 cm. For each surfactant species, 0.6 M NaCl solution and deionized water were used as feed solution and distillate, respectively. For SDBS, an additional set of experiments were performed with a NaCl concentration of 0.3 M. The temperatures of the feed solution and distillate were maintained at 60 and 20 °C, respectively, which resulted in vapor fluxes in a range of 30.5±1.2 L m^{-2} hr^{-1}. Before the addition of surfactants, the system was operated for 10 minutes to develop a stable baseline for vapor flux. The dosing of surfactants resulted in a surfactant concentration of 0.3 mM in the feed solution. During the entire experiment, the mass and conductivity of permeate solution were constantly monitored to determine the water (vapor) flux and salt rejection. To quantify the kinetics of pore wetting, we

measured the breakthrough time defined as the time from the addition of surfactant to the point when the salt rejection dropped to 99. 5%. The selection of a rejection of 99.5% as the criterion for breakthrough, though quantitatively arbitrary to a certain degree, is based on the fact that a small fraction of the membrane pores has been fully wetted through when salt rejection drops below this level. Three replicate experiments were performed for each set of experimental conditions and the experimental results were reported as average values with error bars.

4. Results and discussion

The surface tension of each surfactant solution decreases as the surfactant concentration increases (Fig. 2a). Following the Gibbs adsorption equation (eqn. 1), Γ can be estimated using the slope of the linear regime of the "γ vs. ln (C)" curve before the surfactant concentration reaches the critical micelle concentration, CMC. A more negative slope represents a larger Γ , which suggests that the surfactants occupy less surface area and that it requires more such surfactants to saturate a given surface area. Likewise, a less negative slope indicates that the surfactants are "larger" and fewer of such surfactants are needed to saturate a given surface area (Fig. 2b).

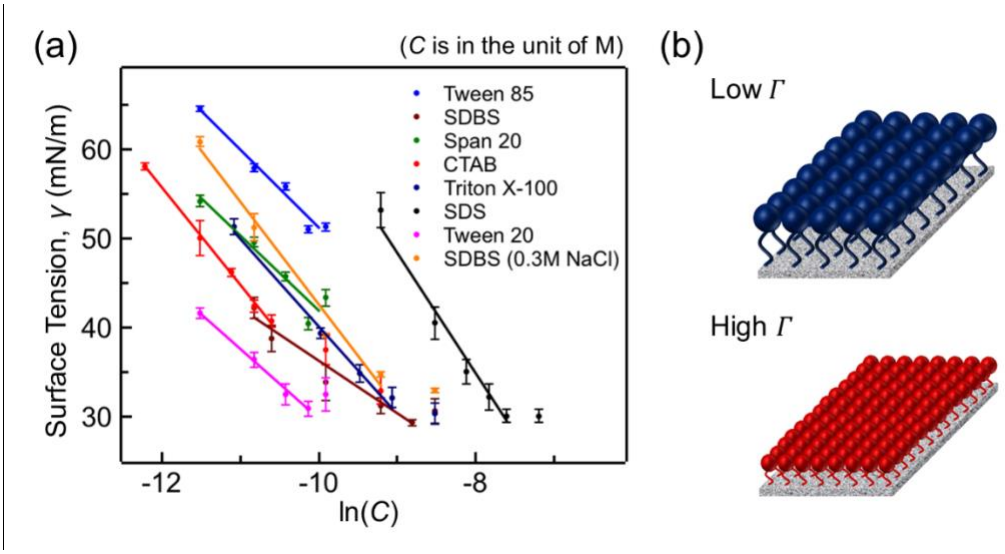

Fig. 2. (a) surface tension, γ, as a function of surfactant concentration for different types of surfactants. The solution temperature was 60 ºC and the default NaCl concentration was 0.6 M. For SDBS, an additional NaCl concentration of 0.3 M was also used. We were interested in the slope of the linear portion of "γ vs. ln (C)" from which the surface excess concentration, Γ, can be determined using equation 1. **(b)** illustration of the concept of surface packing density: compared to "smaller" surfactants (high Γ, bottom), "larger" surfactants (low Γ, top) have a lower surface packing density and require less surfactants to saturate a surface of given area.

The breakthrough time, $t_{wetting}$, determined from the data of the wetting experiments (see Fig. A1 in Appendix), is linearly correlated with Γ in all occasions with the exception of SDS (Fig. 3). Because for ionic surfactants, Γ is strongly dependent on ionic strength [36–38], solutions dosed with the same concentration of SDBS (0.3 mM) but different concentrations of NaCl (0.3, and 0.6 M) have very different Γ which also linearly scales with $t_{wetting}$.

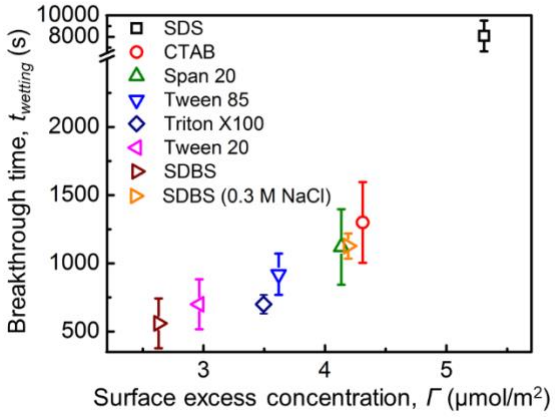

Fig. 3. Wetting breakthrough time, $t_{wetting}$, as a function of Γ estimated from the data in Fig 2(a). In each MD experiment, the inlet temperatures of the feed and permeate streams were maintained at 60 and 20 °C, respectively, which resulted in a water vapor flux of 30.5±1.2 L m^{-2} hr^{-1} in our system. In most cases, the feed solutions were 0.6 M NaCl solutions dosed with different surfactants at 0.3 mM. For SDBS, an additional NaCl concentration (0.3 M) was also tested.

The general linear relationship between $t_{wetting}$ and Γ can be explained by the kinetic model which suggests that the kinetic rate of pore wetting is essentially determined by how fast the pore surface is saturated by the adsorbed surfactants. With this kinetic model, the rate of pore surface saturation is primarily controlled by (1) the rate of surfactant transport from the bulk solution to the wetting frontier, and (2) the surface packing density, which is equivalent to Γ. Because we controlled the surfactant concentration in the bulk solution and the vapor flux to be same in all experiments, the molar flux of all tested surfactants (except SDS) were similar. Therefore, surfactants with low Γ, which are "large" surfactants that saturate a unit area of pore surface with less surfactant molecules, promote faster saturation of the pore surface and thus faster wetting. Similarly, "smaller" surfactants with high Γ saturate the pore surface more slowly because more

surfactant molecules are required to saturate a unit area of surface. Consequently, surfactants with higher Γ resulted in slower wetting with longer $t_{wetting}$.

The argument of similar molar flux (for all surfactants except SDS) in the above discussion implicitly assumes that evaporation-induced convection dominates over the concentration gradient-induced diffusion for the axial transport of surfactants from the bulk solution to the wetting frontier. In fact, the violation of this assumption can be employed to explain the significant deviation of SDS-induced wetting from the linear relationship between $t_{wetting}$ and Γ observed in experiments with other surfactants. As shown in Table A1 in Appendix, the diffusion coefficient of SDS is at least an order of magnitude higher than that of other surfactants.

If we employ the full kinetic model that accounts for both the convective and diffusive contributions to surfactant transport, we can simulate $t_{wetting}$ for different types of surfactants considering both the impacts of the surface packing density and diffusion coefficient. The theoretical predictions based on the full kinetic model match reasonably well with the experimental observations (Fig.4), including the data point measured with SDS. The very good agreement between experimental observations and theoretical predictions does not only apply to different surfactants but also to the same surfactant (SDBS in this case) with different background electrolyte concentrations. The ability of the kinetic model to quantitatively predict the experimental results is quite satisfactory especially considering the many simplifying assumptions (e.g. cylindrical pore geometry) made in the model.

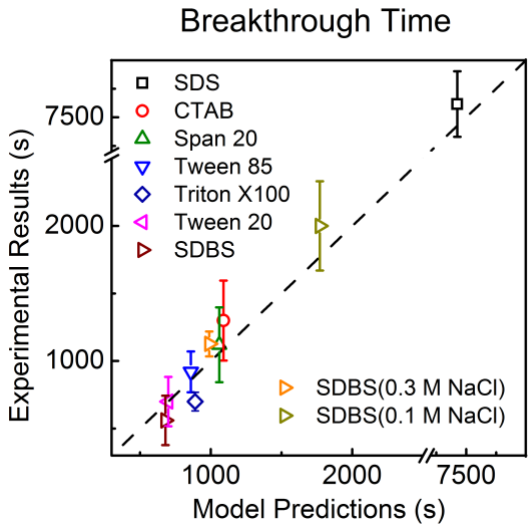

Fig. 4. Theoretical predictions and experimental observations of the wetting breakthrough time, $t_{wetting}$. The coefficient of determination, R_2, is calculated to be 0.97. The theoretical predictions are simulated using the full kinetic model of surfactant-induced pore wetting as reported in our previous publication [25] and briefly summarized in Appendix. The dash line represents perfect match between the theoretical predictions and experimental observations.

According to the kinetic model, the critical concentration (C') at the wetting frontier influences the diffusive transport of surfactants because it affects the concentration gradient. This critical concentration is defined as the surfactant concentration that leads to an LEP' (at the wetting frontier) equal to ΔP. The pseudo force equilibrium assumption demands that the actual surfactant concentration at the wetting frontier be maintained as C'. While C' is difficult to determine experimentally, simulation results using arbitrary C' from 0.01 mM to the CMC of each surfactant suggest that $t_{wetting}$ is virtually independent of C' except for SDS (Table A1). This further affirms our previous argument that convective contribution dominates the transport of all surfactants but SDS to the wetting frontier. For SDS, simulating $t_{wetting}$ requires more accurate estimation of C' by measuring both the surface tension and contact angle of the solution on a smooth PVDF surface, which has been performed experimentally [25]. Randomly selecting a C' for SDS would lead to a huge range of predicted $t_{wetting}$ from 530s to infinity (i.e. the membrane would never be wetted), which highlights the importance of diffusion in the axial transport of SDS in the pore wetting process.

Compared to the strong correlation between Γ and $t_{wetting}$, the correlation between HLB and $t_{wetting}$ appears to be weak (Fig. A3 in Appendix). It may be argued that HLB affects the interaction between surfactants and hydrophobic surface, and thereby influences how fast surfactants adsorb onto pore surface, which in turn impacts the wetting kinetics [26,27]. However, when the interaction is attractive, which is certainly the case for surfactant adsorption onto a hydrophobic surface, adsorption is typically considered to be limited by diffusion [39]. Therefore, even if surfactants with a lower HLB do adsorb onto a hydrophobic surface more strongly, the "stronger" adsorption may not necessarily translate to "faster" adsorption.

More importantly, even if faster adsorption were consequent of a lower HLB, it should have negligible impact on the wetting kinetics based on the wetting model that has been experimentally validated [25]. The length scale for the adsorption of surfactants from the solution in the pore to

the pore surface, which is roughly equal to the pore radius, is significantly smaller than that for the axial transport of surfactants from the bulk solution to the wetting frontier, which is the depth of the partially wetted pore. For this reason, the process of surfactant adsorption onto the pore surface near the wetting frontier is dominantly controlled by the rate at which the surfactants transport from the bulk solution to the wetting frontier, and not by the local adsorption rate that HLB may or may not influence.

It may be possible that HLB has an impact on the surface excess concentration because it can affect the configuration of the adsorbed surfactant macromolecules on surface. In this sense, HLB may indeed have an impact on wetting kinetics via its impact on surface excess concentration. This impact, if indeed present, should have been accounted for in the surface excess concentration that is used in the wetting model.

4. Conclusion

In this study, we have demonstrated that surface excess concentration has a strong influence on the kinetics of surfactant-induced pore wetting. For highly effective surfactants that can significantly reduce surface tension with a very low surfactant concentration, surface excess concentration is arguably the single most important property of a surfactant that affects the wetting kinetics. For less effective surfactants, such as SDS, the diffusion coefficient of the surfactants also has a noticeable impact on the wetting kinetics. These results suggest that the kinetics of surfactant-induced pore wetting is governed by surfactant transport to the wetting frontier.

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Appendix

The results of membrane wetting experiments, summary of model development, and model parameters for different surfactant species can be found in the supporting information.

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Appendix to

Significance of Surface Excess Concentration in the Kinetics of Surfactants-induced Pore Wetting in Membrane Distillation

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Results of Membrane Wetting Experiments

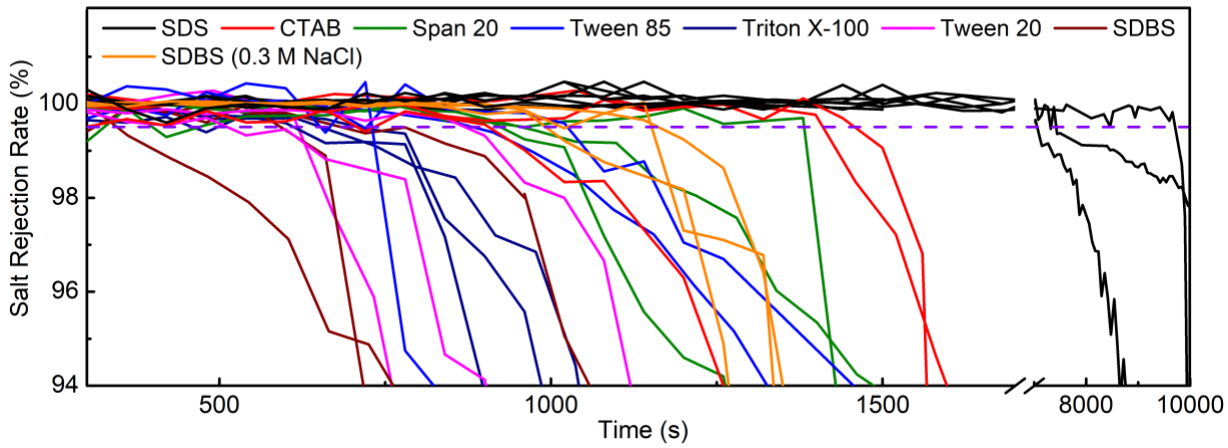

Fig. A1. Salt rejection rate as a function of time in DCMD wetting experiments. Each curve represents the change of salt rejection rate in a wetting experiment, and the color of the curve specifies the surfactant species utilized in the experiment. The purple dash line denotes to a salt rejection rate of 99.5%, which is defined as the criterion for the breakthrough of the membrane pore by salty feed solution. The breakthrough time is attained as the time at which a curve drops below the purple dash line.

Summary of Model Development

The transport of surfactant in a surfactant-induced pore wetting process including convection, diffusion, accumulation, and adsorption is shown in Fig. A2,

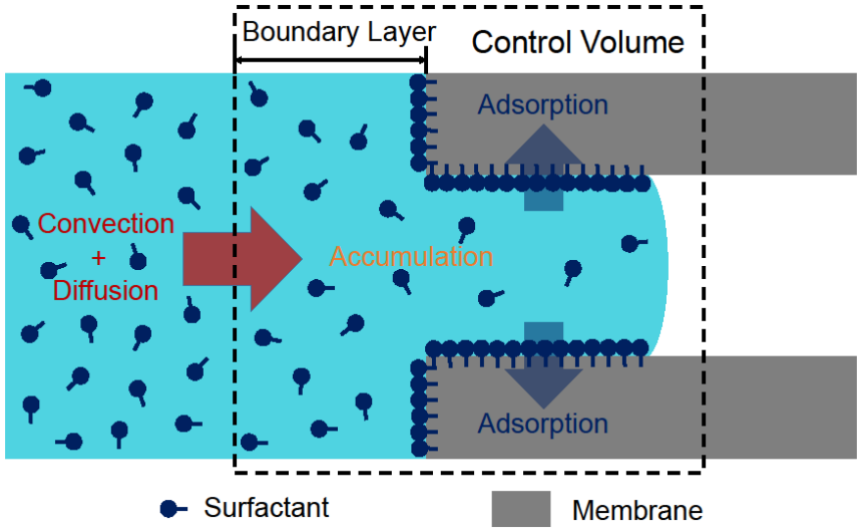

Fig. A2. Schematic of surfactant transport during pore wetting process. During pore wetting process, the surfactant would be absorbed onto the pore surface, which significantly reduces the concentration of surfactant at the wetting frontier. At the meantime, surfactant is continuously transported from the bulk solution to the wetting frontier, which maintains the critical surfactant

concentration (c*) at the wetting frontier. The transport of surfactant is affected by convection and diffusion. Convection is due to the vapor flux and diffusion is because of concentration gradient.

During the wetting process, a force balance of the LEP and transmembrane pressure difference (ΔP) is found at the wetting frontier. If LEP is not balanced with ΔP, an LEP that is lower than ΔP would cause an intermediate wetting process according to Poiseuille flow [1,2], whereas an LEP that is higher than ΔP would not incur the wetting process based on the wetting criterion. Thus, the surfactant concentration at the wetting frontier would be maintained at a critical concentration c*, which corresponds to an LEP equal to ΔP. In the control volume consisting of the boundary layer and the wetted pore (Fig. A2), we can perform mass balance to the surfactant and obtain Eq. A1,

$$\begin{aligned}\left(J_w c_0 - D\frac{\partial c(x,t)}{\partial x}_{x=0}\right)dt &= \int_0^{\delta_b}[c(x,t+dt)-c(x,t)]dx \\ &+ \varepsilon\int_{\delta_b}^{\delta_b+l(t+dt)}[c(x,t+dt)-c(x,t)]dx \\ &+ \varepsilon\int_{\delta_b}^{\delta_b+l(t+dt)}\left[\frac{2}{R}\tau(x,t+dt)(1-\varepsilon)-\frac{2}{R}\tau(x,t)(1-\varepsilon)\right]dx\end{aligned} \tag{A1}$$

Where, J_w is the vapor flux, c_0 is the bulk concentration of the surfactant, D is the diffusion coefficient of surfactant, $c(x,t)$ is the spatial-temporal concentration of surfactant, δ_b is the thickness of the boundary layer hat is estimated to be 15 μm based on Sherwood correlation and the flow conditions [3–5], ε is the porosity of the membrane (0.6), R is the equivalent pore radius (0.225 μm), $\tau(x,t)$ is the spatial-temporal density of the absorbed surfactant on the membrane surface.

In Eq. A1, the left side accounts for convection and diffusion. The first two terms on the right side represent the accumulation of the surfactant in the control volume and the last term stands for the adsorption of the surfactant. The goal is to solve for the wetting distance $l(t)$ as function of t.

To achieve this, first, stepwise adsorption isotherm is assumed,

$$\tau(x,t) = \begin{cases}\tau_{max}, & c(x,t) > 0 \\ 0, & c(x,t) = 0\end{cases} \tag{A2}$$

Where τ_{max} is the maximum adsorption density of surfactant on the membrane surface. This stepwise isotherm is reasonable as it can be derived from Langmuir isotherm with a large equilibrium constant of surfactant that governs the partition of SDS between the pore surface and the solution phase.

Second, we assume pseudo-steady state for surfactant transport in the control volume as the time scale of surfactant transport is significantly small than that of the propagation of the wetting frontier. With this assumption, we can obtain,

$$0 = -J_w\frac{dc}{dx} + D\frac{d^2c}{dx^2}\ (for\ 0 \le x \le \delta_b) \tag{A3}$$

$$0 = -\frac{J_w}{\varepsilon}\frac{dc}{dx} + D\frac{d^2c}{dx^2} \text{ (for } \delta_b \le x \le \delta_b + l(t)) \quad \text{(A4)}$$

with the boundary conditions being $c(0) = c_0$, and $c(\delta_b + l(t)) = c^*$, respectively.

Combing Eqs. A1 to A4, $l(t)$ can be numerically solved as function of t. As the thickness of the membrane was measured to be 180 μm, we can obtain the breakthrough time $t_{wetting}$ with $l(t) = 180\ \mu m$.

Model Parameters for Different Surfactant Species

In each model simulation, the water flux J_w was 30.5 L m^{-2} hr^{-1}, and the bulk concentration for surfactants was 0.3 mM. The maximum packing density of surfactant on the pore surface τ_{max} was approximated using the measured surface excess concentration and the coefficients of determination for surface excess concentrations R^2 were also provided. The diffusion coefficient D of each surfactant was acquired from literatures[6–12].The critical concentrations C′ for SDS was estimated using the following equation with an LEP of 6 kPa (i.e. the transmembrane pressure in the experiments)

$$\text{LEP} = -\frac{2\gamma(C')\cos(\theta(C'))}{R}$$

where $\gamma(C')$ and $\theta(C')$ are the surface tension of the solution and its contact angle on a PVDF surface, respectively, both being a function of C' (ref [25] in the main text for more details). For other surfactants, we performed the simulations using C' from 0.01 mM (extremely low) to the CMC of the surfactants from the surface tension measurements. We note that LEP does not change when C' is beyond CMC because $\gamma(C')$ and $\cos(\theta(C'))$ becomes constant when C' is beyond CMC. We find that for all other surfactants except SDS, the choice of C' within this range does not have any appreciable impact on the simulated t_{wetting} because diffusion is unimportant compared to convection in the axial transport of these surfactants. A summary of surface excess concentration, Γ, coefficient of determination R^2 (for Γ), critical concentration, C', diffusion coefficient, D, and the simulated t_{wetting} for different surfactant species are shown in **Table A1**.

Table A1. The parameters for model prediction of pore wetting by different surfactant species (corresponding to Fig. 3 in the main text)

Surfactant Species	Γ ($\times 10^{-6}\ mole\ m^{-2}$)	R^2 (for Γ)	C' (mM)	D ($\times 10^{-10}\ m^2\ s^{-1}$)	t_{wetting} (C'=0.01 mM)	t_{wetting} (C'=CMC)
SDS	5.31	0.977	0.36	7.3	7130 (C'=0.36 mM)	
Triton X100	3.50	0.990	0.01-0.2	0.4	890	890
Tween 20	2.96	0.998	0.01-0.05	0.75	700	700
Tween 85	3.62	0.975	0.01-0.05	0.7	860	860
Span 20	4.13	0.989	0.01-0.05	0.12	1060	1060
CTAB	4.31	0.999	0.01-0.05	0.39	1090	1110
SDBS (0.6 M NaCl)	2.62	0.945	0.01-0.2	0.2	680	680
SDBS (0.3 M NaCl)	4.19	0.987	0.01-0.2	0.8	980	990

Membrane Pore Wetting Breakthrough Time as a Function of HLB

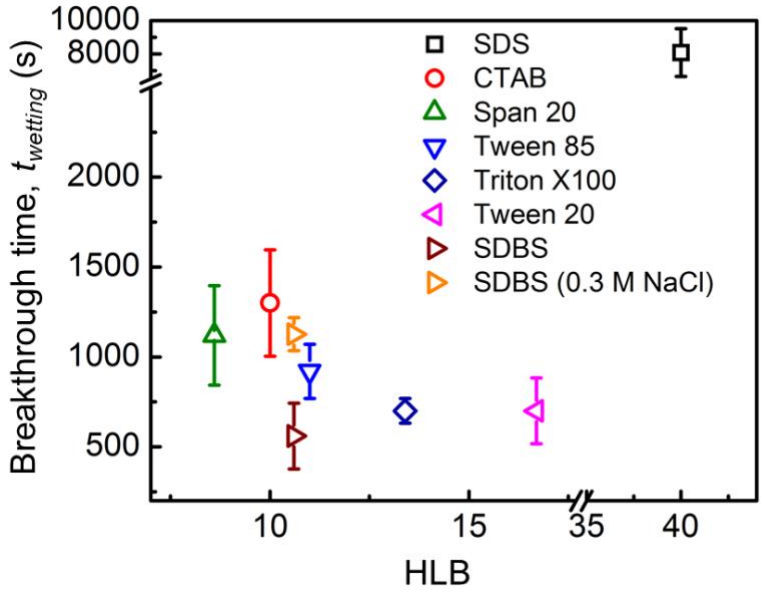

Fig. A3 Wetting breakthrough time, $t_{wetting}$, as a function of HLB

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