How Do Surfactants Control the Agglomeration of Clathrate Hydrates?

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ABSTRACT: Clathrate hydrates can spontaneously form under typical conditions found in oil and gas pipelines. The agglomeration of clathrates into large solid masses plugs the pipelines, posing adverse safety, economic, and environmental threats. Surfactants are customarily used to prevent the aggregation of clathrate particles and their coalescence with water droplets. It is generally assumed that a large contact angle between the surfactant-covered clathrate and water is a key predictor of the antiagglomerant performance of the surfactant. Here we use molecular dynamic simulations to investigate the structure and dynamics of surfactant films at the clathrate–oil interface, and their impact on the contact angle and coalescence between water droplets and hydrate particles. In agreement with the experiments, the simulations predict that surfactant-covered clathrate–oil interfaces are oil wet but super-hydrophobic to water. Although the water contact angle determines the driving force for coalescence, we find that a large contact angle is not sufficient to predict good antiagglomerant performance of a surfactant. We conclude that the length of the surfactant molecules, the density of the interfacial film, and the strength of binding of its molecules to the clathrate surface are the main factors in preventing the coalescence and agglomeration of clathrate particles with water droplets in oil. Our analysis provides a molecular foundation to guide the molecular design of effective clathrate antiagglomerants.

1. INTRODUCTION

Gas clathrate hydrates are nonstoichiometric compounds in which guest molecules such as methane, propane, and carbon dioxide are entrapped within a crystalline network of water cages.1–8 On the one hand, clathrate hydrates have promising applications in energy recovery and gas storage,9,10–15 as they are ubiquitous in deep ocean sediments and permafrost environments and estimated to be the most abundant hydrocarbon energy source.16,17 On the other hand, the high pressure, low temperature, and presence of water in subsea oil and gas pipelines provide ideal conditions for the formation of clathrates.1,18,19 Agglomeration of these hydrate particles can result in plugging of the pipelines, posing economic losses, as well as safety and environmental threats.10–24 Controlling the growth and agglomeration of hydrate particles is key for flow assurance.

Economic and safety concerns caused by pipeline plugging have driven the search for effective inhibitors that delay or prevent the nucleation, growth, or agglomeration of clathrate aggregates.19,25,26 The traditional way of preventing hydrate plugging involves the addition of thermodynamic inhibitors (TI), such as methanol and ethylene glycol, that shift the equilibrium conditions, such that the formation of clathrate hydrates is no longer favorable.25,27,28 However, large quantities of these chemicals are needed to prevent the formation of clathrates, which makes this strategy economically costly and environmentally risky.25,29 Use of low dosage hydrate inhibitors (LDHIs) provides a cost-effective means to prevent the formation and agglomeration of clathrate hydrates in pipelines.25,30,31 LDHIs are broadly divided into two types, depending on their mode of action: kinetic hydrate inhibitors (KHIs) and antiagglomerants (AAs). KHIs delay the formation of clathrate hydrates long enough for safe transportation of oil without blockage under moderate supercooling conditions.25 Antiagglomerants are surface active molecules that strongly adsorb to the surface of hydrate particles.25,32 AAs provide an appealing way to ensure flow in gas pipelines operated at high subcooling conditions,3,26 for which KHIs are not effective.24 By dispersing the hydrate particles in the oil phase, AAs produce a slurry that ensures flow through the pipelines.

The agglomeration of gas hydrates is a consequence of a series of processes: nucleation of the hydrate, its growth, and the cohesion of hydrate particles.3,25 These processes lead to the formation of large aggregates that are responsible for the plugging of pipelines.25,26 Arresting one of these processes should disrupt the cascade of events leading to the blocking. The interaction and adhesion between a hydrate particle and a water droplet are considered to play an important role in the agglomeration process.36,37 The consensus is that the gas-saturated water droplet grows clathrates once in contact with the crystal. The subsequent attachment and crystallization of more water droplets ultimately result in the formation of large agglomerates.20

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A widely used class of AAs includes quaternary ammonium surfactants.22 The quaternary ammonium center is typically functionalized with n-butyl or n-pentyl groups and one or two long alkyl tails. Molecular simulations indicate that bulky quaternary ammonium surfactants form an ordered AA long alkyl tails. Molecular simulations indicate that bulky \( \gamma \) fi AA methane to the clathrate surface.38,39 Therefore, the formation of water indicates that linear alkanes can intercalate with the oil phase, as interfacial tensiometry and ellipsometry experiments indicate that linear alkanes can intercalate with the surfactants to form a crystalline interfacial monolayer at the water–alkane interface.58,41,42 and may be able to do so also at the clathrate–oil interface. It has been proposed that surfactants adsorbed to the hydrate surface prevent the contact between hydrate particles and water droplets by changing the wettability of the hydrate surface from water wet to oil wet.38,55,57 A recent study of four AAs found a correlation between increasing contact angle and decreased adhesion force between hydrate particles.21,37,45 It is not known, however, whether in general a high contact angle is sufficient to ensure good AA activity.

The process of coalescence of a water droplet with a surfactant-covered clathrate involves a free energy barrier, as schematized in Figure 1. The process involves the net change from clathrate–surfactant–oil plus water–oil interfaces to clathrate–water plus water–surfactant–oil interfaces. If the costs of the clathrate–surfactant–oil and water–surfactant–oil interfaces are similar, the coalescence would have a driving force proportional to the difference between the cost of the water–clathrate and water–oil interfaces, \( \gamma_{\text{clathrate-water}} - \gamma_{\text{water-oil}} \). Literature values for the free energy of the clathrate–water interface, \( \gamma_{\text{water-clathrate}} = 33 \pm 4 \text{ mJ m}^{-2} \),44,45 and the dodecane–water interface, \( \gamma_{\text{water-oil}} = 53 \text{ mJ m}^{-2} \),46,47 indicate that the driving force for coalescence of the clathrate and water droplet in oil is favorable, \( \gamma_{\text{water-clathrate}} - \gamma_{\text{water-oil}} \approx -20 \text{ mJ m}^{-2} \). Free energy calculations of coalescence of nanodroplets and surfactant-covered clathrate nanoparticles support this conclusion.54 In the presence of an excess of surfactant concentrations, both the clathrate surface and the water droplet could be covered by surfactants, decreasing the driving force for coalescence. This analysis indicates that the surfactants do not necessarily make the coalescence thermodynamically unfavorable: their main role is to slow down the kinetics of this process by decreasing the contact between water and the clathrate and increasing the magnitude of the barrier for water penetration. Understanding how the structure of the surfactants and their similarity to the oil phase impact these properties is key for predicting the efficiency of surfactants as AAs.

Here we use molecular dynamics simulations to investigate the factors that control the thermodynamics and kinetics of coalescence of water with surfactant-covered and bare clathrate surfaces. In sections 3A–C we determine the binding free energy, mobility, and structure of surfactants at clathrate–alkane interfaces. In section 3D we compute the contact angles of water and alkanes at clathrate–alkane interfaces with and without surfactants. In section 3E we investigate the coalescence between water droplets and surfactant-covered clathrates, determine whether a high contact angle is sufficient to prevent the aggregation of water and surfactant-covered clathrate particles, and use the results of sections 3A–D to elucidate the role of surfactants in controlling the agglomeration of clathrate hydrates and water droplets dispersed in an oil phase.

2. METHODS

A. Simulation Settings. We perform molecular dynamics (MD) simulations using LAMMPS.48 The equations of motion are integrated with the velocity Verlet algorithm using a time step of 5 fs. The simulation cells are periodic in the three Cartesian directions. We perform the simulations in the isobaric isothermal (NpT) ensemble, except when a vapor phase is involved, in which case we keep the dimensions of the cell fixed in the direction perpendicular to the clathrate-vapor interface. The temperature and the components of the pressure tensor are controlled independently with the Nose-Hoover thermostat49 and barostat50 with time constants 2.5 and 12.5 ps, respectively. The simulations are evolved for 200 ns, except when otherwise indicated.

B. Models. We model the clathrate hydrates with the monatomic water model mW,52 which represents each water molecule by a single particle that interacts through short-range two- and three-body potentials. The mW model has been extensively validated to reproduce the structure,44,51–58 thermodynamics,44,51,55,59–66 and interfacial properties51,54,67 of clathrate hydrates. Methane is represented with the monatomic M model.71 The equilibrium melting temperatures for the M filled sl and sII hydrates are 302 and 301 K at 100 bar, respectively.72,73 The guest free sl and sII hydrates have equilibrium melting points of 245 and 252 K at 1 bar.74 The alkanes are modeled at the united atom (UA) level with the UA-PYS force field,75 which represents each CH3 and CH2 group by a single particle that interacts through Lennard-Jones potentials. The interactions between the UA methyl and methylene groups with mW water are modeled with Lennard-Jones interactions parametrized in ref 75. The carbon backbone of the alkanols is also modeled with UA-PYS and
the hydroxyl group with the mW model,\textsuperscript{51} with cross-interactions between the alkane groups and either water or OH groups modeled with Lennard-Jones potentials with the parameters of refs \textsuperscript{68, 76–78}.

We prepare two-phase clathrate–alkane systems in which the clathrate is either methane-filled or guest-free sI hydrate exposing the [100] crystallographic plane, or guest-free sII hydrate exposing the [001] face to the vapor or alkane phase. The alkane consists of either n-pentane, n-hexane, or n-dodecane. The [100] face of sI is the slowest growing face of the crystal,\textsuperscript{54} and hence it is expected to be the dominant among those exposed to the fluid.

The simulation cells used in section 3A to investigate the adsorption and binding free energy of dodecanol to the sI clathrate–pentane interface contain 2820 water molecules in the sI clathrate phase filled with 427 methane molecules (100\% occupancy of small and large cages), 1 dodecanol molecule, and 1000 pentane molecules. The dimensions of the cells are 11.8 nm \times 4.7 nm \times 4.7 nm. We call this “box 1.” In section 3B we use a simulation box with dimensions of 11.8 nm \times 4.7 nm \times 4.7 nm to analyze the diffusivity of the dodecanol molecules. The box contains 2308 water molecules, 1 dodecanol molecule, and 1000 pentane molecules for the water–pentane systems. We use box 1 to calculate the diffusivity of a dodecanol molecule at the clathrate–pentane interface. The simulation cell used to calculate the free energy between two dodecanol molecules contains 2308 water molecules in the guest free sII clathrate phase, and two dodecanol molecules in 1000 pentane molecules. In section 3C we use the same configuration of methane-filled clathrate of box 1, in contact with different alkanes and alkanols: pentane, hexane, and dodecane as the alkane oil and hexanol and dodecanol as the alkanol. The simulation cells that contain dodecane, hexane, and pentane as the oil phase contain 512 dodecanol molecules, 835 hexane molecules, and 1000 pentane molecules, respectively. The number of dodecanol and hexanol molecules used are 49 for the 2.22 nm\textsuperscript{2} and 98 for the 4.43 nm\textsuperscript{2} surfactant density. The simulation cells used to investigate the wetting of the clathrate surface at the clathrate–vapor interface in section 3D and 3E contain 232 surfactants in the monolayer in contact with 1000 water molecules, 5640 molecules in the sI clathrate phase, and 854 guest molecules. The simulation cells for the investigation of the wetting of a water droplet at the clathrate–dodecane interface contain 98 dodecanol molecule, 1042 dodecane molecules, 1000 water molecules, and 5640 molecules in the clathrate phase. The dimensions of the cells are 13.4 nm \times 9 nm \times 4.7 nm. The dodecanol monolayers in the sections 3D and 3E are prepared with the same area per molecule reported in the experiments\textsuperscript{79} for C\textsubscript{16}OH, equilibrating the systems to get the final configuration.

C. Analysis. Diffusivity Calculation. We compute the diffusion coefficients of a single dodecanol molecule at the guest free–sII–clathrate–pentane interface at 248 K and 1 bar, 4 K below the melting point of this crystal.\textsuperscript{74} The self-diffusion coefficient \(D\) is determined from the Einstein relation in two dimensions, \(\langle r^2(t) \rangle = 4Dt\), where \(t\) is the time elapsed and \(\langle r^2(t) \rangle\) is the mean squared displacement of OH group of the dodecanol in that time interval. The diffusion coefficient is computed averaging over 100 ns simulations, with configurations saved every 250 ps.

Free Energy Calculations. We use umbrella sampling\textsuperscript{80} and WHAM\textsuperscript{81} analysis to compute the free energy of binding of a dodecanol molecule to the methane filled sI clathrate surface in equilibrium with n-pentane at 100 bar at 265, 275, and 285 K. The umbrella sampling simulations are performed using a harmonic restraint with a force constant \(k = 2\) kcal mol\textsuperscript{−1} Å\textsuperscript{−2} to restrain the distance between the center of mass of the hydroxyl group and a tethered point that corresponds to the position of the OH when the dodecanol is bound to the surface of the clathrate. The bound reference configuration is obtained from a 500 ns simulation in which one dodecanol spontaneously binds to the clathrate–dodecane interface. We perform simulations sampling distances from 0 to 15 Å, every 0.5 Å, using 30 independent umbrella windows, each equilibrated for 100 ps and then run for 10 ns that are stored for the analysis. We compute the entropy of association, \(S = −(\partial G/\partial T)_p\), from the finite difference of the free energies with temperature at the bottom of the free energy well, and the enthalpy of binding, \(H, f r o m H = G + TS\).

We compute the free energy of attraction between two dodecanol molecules at the guest-free sI clathrate-pentane interface at 248 K and 1 bar. We first equilibrate the simulation cell for 5 ns and then collect statistics from a very long, 1 \(\mu\)s simulation from which we compute the radial distribution function between the OH groups of the two surfactants in the plane of the surface, and compute from it the potential of mean force as a function of the distance \(r\) between the head groups, \(\Delta G(r) = −RT \ln g(r)\).

Contact Angles. Contact angles of a water droplet at the clathrate–alkane interface with and without surfactants are computed from the density profile of the water droplet, averaged over 200 ns simulations at 277 K. We use a cylindrical water droplet that is periodic along the cylinder axis, because that configuration ensures that the line tension of the three-phase boundary does not affect the measurements. To compute the contact angle \(\theta\), we fit the density profile of the water droplet to a second order polynomial, as in ref \textsuperscript{82}. We compute the error bar in \(\theta\) as the standard deviation of the angles fitted from each simulation.

3. RESULTS AND DISCUSSION

Quaternary ammonium surfactants are widely used as antiagglomerants.\textsuperscript{22,25} Recent simulation studies have produced important insights into the AA activity of these surfactants using all-atom models with long-range electrostatic interactions.\textsuperscript{32,83} The computational cost of these models, however, limits their accessibility to processes that require larger simulation boxes and occur on time scales above \(\approx 100\) ns. Our group has previously shown that it is possible to model ions with short-range interactions, including solutions of tetraalkylammonium chloride.\textsuperscript{84} As the coarse-grained representation of ionic species has not yet been validated for water–oil interfaces, here we use nonionic alkanols as model surfactants and discuss the implications of our results and analysis for ionic surfactants. Although alkanols are not used as sole components in AA formulations, because of their limited solubility in high water cut oils, they are used as cosurfactants to decrease the amount of AAs used in water–oil mixtures.

A. Adsorption of Surfactants to the Clathrate–Oil Interface Is Driven by Enthalpy. Surfactants can bind to both clathrate–water\textsuperscript{21,12,13,66,83,86,87} and clathrate–oil\textsuperscript{51,37,83} interfaces. Binding of surfactants to clathrate–water interfaces promotes the nucleation\textsuperscript{38} and could stall the growth\textsuperscript{40,88} of clathrate hydrates. Binding of surfactants to clathrate–oil interfaces is used to prevent the agglomeration of clathrate.
particles and their coalescence with water droplets.\textsuperscript{22,25,35,89} We investigate how a model surfactant, dodecanol, binds to the surfaces of guest-free and methane-filled sl and sI hydrates in contact with \textit{n}-pentane. The alkane is liquid under the conditions of the simulations, which are 277 K and 100 bar for the methane hydrates and 248 K and 1 bar for the guest-free ones. These temperatures are 25 and 4 K below the corresponding equilibrium melting points of these hydrates, respectively.\textsuperscript{27,74} The simulations indicate that dodecanol binds to the clathrate surface exclusively via its hydroxyl group (see snapshot inset in Figure 2). The hydrophilic headgroup hydrogen bonds to water molecules at the clathrate surface, where it has an average of three water neighbors, but does not penetrate inside the half cages\textsuperscript{83} exposed at the clathrate surface. This is not unexpected, as solvation of an OH group inside a water cage would lead to its collapse. The hydrophobic tail of the alcohol is solvated by the alkane and its occupancy—filled with methane or guest-free—has no bearing on the mode of binding of dodecanol to the clathrate surface.

It has been proposed that surfactants that bind strongly to the clathrate—oil interface are effective AAs.\textsuperscript{32} We compute the free energy of adsorption of a single dodecanol to the clathrate—pentane surface to quantify the strength of the binding. We find that the free energy of binding of dodecanol to the [100] plane of methane filled sl hydrates is $\Delta G = -8.5$ kcal mol$^{-1}$ at 275 K and 100 atm (Figure 2). The simulations probably underestimate the strength of binding of the alcohol to the clathrate surface, as we have assumed that the interactions between water and OH are identical to those between water molecules, while \textit{ab initio} CCSD(T) indicates that the average strength of the optimized hydrogen bond between water and alcohol is 13 and 10% higher than for water—water, for ethanol and methanol, respectively.\textsuperscript{80} A stronger interaction between water and the OH is also supported by the negative excess enthalpy of mixing of water and alcohols in experiments.\textsuperscript{82} We do not expect, however, that the interaction between the alcohols and the clathrates will be as strong as for ionic surfactants. For comparison, the free energy of adsorption of quaternary ammonium salts, the most commonly used AAs, has been reported to be between $\sim -3$ and $-36$ kcal mol$^{-1}$;\textsuperscript{83} their strong affinity has been attributed to the solvation of the ammonium cation in the premelted water layer at the interface.\textsuperscript{83} Nonionic surfactants like dodecanol, on the other hand, adsorb through hydrogen bonding to the clathrate surface. We find that the adsorption of the alcohol to the clathrate—oil interface is driven by enthalpy: at 275 K and 100 bar the enthalpic contribution to the free energy is favorable by $-12.9$ kcal mol$^{-1}$, while the entropic contribution is unfavorable by $4.4$ kcal mol$^{-1}$. We interpret that the main contribution to the decrease of entropy upon binding originates in the loss of translational entropy of the surfactant as it moves from the bulk hydrocarbon to the surface where, we show in section 3B below remains highly mobile. The enthalpy-driven binding of dodecanol to the clathrate—alkane interface contrasts with the binding of the same surfactant to the clathrate—water interface, which is almost equally strong but driven by the entropy of dehydration of the alkyl groups as they adsorb into the half-cages at the clathrate surface. We expect that adsorption of quaternary ammonium surfactants to the clathrate—alkane interface in low water-cut environments is also driven by enthalpy, dominated by the enthalpy of hydration of the ions at the clathrate surface.

### B. Dilute Surfactants Are Highly Mobile at the Clathrate—Oil Interface
Dodecanol displays high mobility at the clathrate surface when its coverage is low, despite its strong binding to the clathrate—alkane interface. The surfactant molecules diffuse by jumping between neighboring hydrogen bonding sites at the crystal surface, without ever desorbing from the interface. The diffusion coefficient of a single dodecanol at the clathrate—pentane interface is 3 times lower than at the interface between liquid water and pentane. This is consistent with the higher mobility of quaternary ammonium surfactants at water—oil than clathrate—oil interfaces.\textsuperscript{32} These results suggest that the crystallinity of the clathrate surface is deleterious for the mobility of the adsorbed surfactants.

The mobility of dodecanol at the clathrate—alkane interface, however, is orders of magnitude faster than at the clathrate—water interface, to which dodecanol binds through insertion of the alkyl tail into half-cages exposed at the surface.\textsuperscript{68} We find that a dodecanol molecule takes less than 1 ns to move between two consecutive cages at the clathrate—pentane interface, while the same surfactant at the clathrate—water interface does not move between adjacent cages within microsecond simulations.\textsuperscript{68} This difference arises from the distinct mode of binding of dodecanol to the clathrate—oil and clathrate—water interfaces: the alkyl end of the surfactants is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Free energy of binding of dodecanol to the methane-filled sl clathrate in contact with pentane at 100 bar and 265 K (blue line), 275 K (red line), and 285 K (green line) as a function of the distance $r$ from the clathrate surface. The origin, $r = 0$, locates the plane where the density of water is 50% of the average water density in the clathrate (shown here, for reference, in arbitrary units with a light gray line). Dodecanol molecules adsorb strongly to the clathrate surface driven by the enthalpy of formation of hydrogen bonds between the OH of the alkanol and the surface of the clathrate. The inset shows a snapshot of the simulation cell in the bound state, in which water in the clathrate is shown with green sticks, methane with cyan balls, the alkane with gray sticks, the hydroxyl group of dodecanol with a red ball, and the alkyl backbone with blue balls.}
\end{figure}
adsorbed deeply into the half-cages at the clathrate–water interface,\(^{66}\) resulting in a high barrier to move from cage to cage. The higher mobility of dodecanol at the clathrate–oil interface allows for fast reconfiguration of surfactants at the oil surface, which we expect to be important for healing defects in the interfacial layer and preventing water penetration.

Figure 3 shows the free energy of attraction between two dodecanol molecules at the sII clathrate–pentane interface at 4 K below the melting point of the hydrate. The results are qualitatively the same for the sI clathrate. The free energy profile consists of two distinct minima that correspond to the contact pair (CP) and solvent separated pair (SSP). The two adsorbed dodecanol molecules are hydrogen bonded to each other in the contact pair, whereas the two hydroxyl groups are separated by a water molecule in the SSP. The roughness of the free energy profile is not due to insufficient sampling; it reflects the inherent granularity of the clathrate surface that results from the presence of incomplete cages and its low degree of premelting at the conditions of our analysis. Less than a full liquid-like layer exists on the clathrate surface at the temperature of the simulations, 4 K below the equilibrium melting point of the guest-free sII clathrate. In agreement with previous reports for clathrates\(^{93,94}\) as well as for ice\(^{70,95,96}\), we find that the premelted layer on the clathrate–vapor and clathrate–alkane interfaces increases on approaching the equilibrium melting temperature. We expect that, as the premelted layer thickens on approaching the melting point of the clathrate, the free energy profile will become smoother at distances beyond the SSP. We note that the free energy of attraction at the CP and SSP configurations is less than the thermal energy (\(RT \approx 2 \text{ kJ mol}^{-1}\)). This implies that dodecanol adsorbed to the clathrate–alkane interface experiences not only high mobility, but also very low attraction to other surface-adsorbed dodecanol molecules in the dilute surface coverage (i.e., surface gas) regime. We interpret that the low attraction arises from the inability of weak van der Waals forces, which also exist between the surfactants and the alkane, to compensate for the loss of translational and configurational entropy that would result from pairing the surfactants.

C. Dodecanol Induces Orientational Ordering of Dodecanol at the Clathrate–Dodecane Interface. We now turn our focus to conditions that lead to high-density coverage of surfactants at the clathrate–alkane interface, to assess whether the similarity between the chain length of the surfactants and the alkanes in the oil phase impacts the formation of an ordered monolayer at the interface. In all cases, we model the methane-filled sI clathrate in contact with the alkane fluid at 277 K and 100 bar. These conditions favor hydrate formation and are common in subsea oil pipelines.\(^{16}\) We consider three surfactant–alkane mixtures: dodecanol in dodecane, dodecanol in pentane, and hexanol in hexane.

We first study how dodecanol interacts with the clathrate–dodecane interface at surfactant densities corresponding to 13%, 30%, and 41% surface coverage, where we consider that the 100% coverage corresponds to that of the crystal monolayer in experiments, 5.319 nm\(^{-2}\).\(^{2,76,79}\) We find that all surfactants, initially dissolved in the alkane, migrate to the clathrate surface. Dodecane intercalates with the surfac-adsorbed dodecanol with coverage 41% (but not 30% or 13%), to form an interfacial monolayer that completely covers the surface of the clathrate (Figure 4a). The dodecane and

Figure 3. Free energy profile as a function of the distance between the OH groups of a pair of dodecanol molecules adsorbed at the empty sII clathrate–pentane interface at 248 K, 4 K below the melting temperature of this crystal. The attraction free energy between the adsorbed surfactants is comparable to the thermal energy, \(RT\). The two minima shown in the free energy curve correspond to the contact pair, at 2.5 Å, and the solvent separated pair, at 5 Å.

Figure 4. Dodecanol and dodecane form mixed compact monolayers at the clathrate–dodecane interface. (a) Side view of the two-phase methane clathrate–dodecane simulation cell showing the equilibrium interfacial film consisting of intercalated dodecanol and dodecane molecules at 277 K and 100 bar. (b) Top view of a starting configuration with a patch of pure dodecanol monolayer at clathrate–dodecane interface. (c) Dodecanol and dodecane initialized as in (b) spontaneously rearrange to form an intercalated monolayer in which both surfactant and alkane are aligned. In all the representations, water is shown with green sticks, methane guest with cyan balls, the alkane in gray, the hydroxyl groups of the surfactants with red balls, and the alkyl chain of the surfactants with blue balls. The surface coverage of dodecanol and alkane molecules is 95% of the one of a crystalline monolayer.
dodecanol molecules in the monolayer are mixed (Figure 4a), forming a dense liquid with a total surface density 95% of that of the crystal. All molecules in the interfacial monolayer are aligned almost perpendicular to the surface. This indicates that high concentrations of dodecanol induce surface freezing of the orientation—but not the positions—of the alkanes at the clathrate interface. We find that ordering of dodecan by dodecanol is only achieved if the two species are mixed at the interface: the interfacial alkanes remain orientationally disordered if the dodecanol is clustered in a compact monolayer surrounded by alkanes (Figure 4b). That surface-segregated system spontaneously evolves toward mixed dodecanol and aligned dodecan at the surface (Figure 4c). Surface freezing of alkanes induced by surfactants has been also inferred from the experimental change in surface tension with temperature (i.e., the surface entropy) of the water–tetradeacne interface in the presence of surfactant cetyltrimethylammonium bromide (CTAB).41,42,97 Bui et al. have observed ordering of alkanes within the intercalated interfacial film in simulations of \(N,N'-((hexyl-2',1-diyli))ditiodecanamide chloride surfactants at the clathrate–oil interface.\)

In sections 3D and 3E below we show that sub-monolayer densities of dodecanal intercalated by alkanes create a barrier for the coalescence of water and the clathrate.

It has been proposed that compatibility of the chain lengths in surfactants and alkanes is key for the formation of an aligned interfacial film at the clathrate–alkane interface.\(^\text{38}\) To test this hypothesis, we investigate the ordering of dodecanol at the sI methane–pentane interface at 277 K and 100 bar. The dodecanol dissolved in pentane and— the same as in dodecan—the surfactant transfers to the clathrate–alkane surface. Different from dodecanol, however, pentane does not intercalate with dodecanol: the alkanol forms a pure compact monolayer that covers 41% of the surface (Figure 5a). We find that the patch of dodecanol does not mix with the surrounding pentane, irrespective of whether the dodecanol monolayer is crystalline or liquid. The lack of mixing between dodecanol and pentane at the clathrate–pentane interface indicates that the gain in van der Waals interactions that would arise from aligning (pairs of) pentane molecules with the dodecanol to form a mixed aligned monolayer does not yet compensate for the loss of translational entropy that this process entails. The two components do not mix in the simulations even when the temperature is 297 K, close to the 304 K melting temperature of the methane sI clathrate, although they are fully mixed in simulations of dodecanol at the water–pentane interface at 340 K. The mixing, however, does not result in alignment of the alkanes at the interface. The mixing transition may occur at lower temperatures in experiments, as dodecanol and hexane are already mixed at the water–hexane interface in experiments at 281 K and 1 bar.\(^\text{98}\) Our results indicate that high dodecanol densities and low temperatures are needed to form an ordered monolayer that can act as a barrier to prevent coalescence between hydrate particles and water droplets in light, short chain alkane oil.

The results discussed in the previous paragraphs raise the question of whether it may be possible to form a compact aligned barrier of short-chain alkanols intercalated with short-chain alkanes as a deterrent for clathrate agglomeration in light oils. To this end, we investigated whether hexanol forms an aligned interfacial layer at the clathrate–hexane interface, considering two average surface densities of the alkanol: 2.22 nm\(^{-2}\) (as in the 41% coverage of dodecanol studied above) and 4.43 nm\(^{-2}\). The simulations are performed at 277 K and 100 bar at the interface between sI methane clathrate and hexane. We find that all hexanol molecules absorb to the surface, but—different from the results for dodecanol—the tails of hexanol are not aligned for either surfactant densities (Figure 5b). Bui et al. found the same phenomena where short chain surfactants that contain a quaternary and an amide headgroup do not form an ordered monolayer at the clathrate interface.\(^\text{38}\) Consistent with that study, we find that even high concentrations of short surfactants do not result in the formation of a compact monolayer at the clathrate interface. The simulations indicate that both the pure and mixed hexanol–hexane monolayers are not compact. We show in section 3E below that a monolayer of short surfactants provides a poor barrier for the penetration of water.

In summary, we find that compatibility of the length of alkane and surfactant does not ensure the formation of ordered interfacial monolayers. Only for the longer, dodecanol in dodecane mixtures, the alkane can be interdigitated into the monolayer to form an orientationally ordered compact barrier. In the next sections we investigate the wetting states of clathrates with and without surfactants and how the surfactants act as a barrier against the coalescence of clathrate particles and water droplets.

D. Surfactant Monolayers Change the Wetting State of the Clathrate

Experiments indicate that the wettability of the clathrate surface changes from water-wet to oil-wet in the presence of naturally occurring surfactants in crude oil.\(^\text{12}\) It has been suggested that hydrate agglomeration could be prevented...
by changing the water wettablility of hydrates, thereby preventing the coalescence of hydrate particles and water droplets.\textsuperscript{38,37} Here we use molecular simulations to determine the contact angle of a water droplet at the clathrate–dodecane, clathrate–surfactant–dodecane, and clathrate–dodecanol–vapor interfaces, as well as the contact angle of a dodecane droplet at the clathrate–surfactant–vapor interface. The clathrate is always sil filled with methane, and the simulations are performed at 277 K and 100 bar with a 5.22 nm\textsuperscript{2} surface coverage for the pure dodecanol monolayer and 4.43 nm\textsuperscript{2} for the mixed aligned monolayer that consist of dodecanol and dodecane. We find that water wets the clathrate–dodecane interface with a contact angle $\theta = 34 \pm 2^\circ$ (Figure 6a) in agreement with previous assumptions\textsuperscript{35,43,99,100} and experiments that report $\theta = 29^\circ$ for water at the clathrate–freon interface.\textsuperscript{68} We use the Young equation,\textsuperscript{101} $\cos \theta = (\gamma_{c-o} - \gamma_{w,o})/\gamma_{w,c}$ and the surface tensions of the clathrate–water interface, $\gamma_{w,c} = 33 \pm 4$ mJ m\textsuperscript{-2}\textsuperscript{2,44,45} and the dodecane–water interface, $\gamma_{w,o} = 53$ mJ m\textsuperscript{-2}\textsuperscript{2,46,47} to determine that the surface free energy of the clathrate–dodecane interface is $\gamma_{c,o} = 76.9 \pm 2$ mJ m\textsuperscript{-2}. To our knowledge, this is the first determination of the free energy of a clathrate–alkane interface using molecular simulations. The same approach could be used to obtain the surface free energies of clathrate with other fluids.

The clathrate–dodecane interface covered by the surfactant monolayer is super-hydrophobic: the simulations indicate that $\theta = 180^\circ$; i.e., water does not wet at all the surfactant-covered clathrate. We find the same contact angle for clathrate covered with a pure dodecanol monolayer or with a monolayer made of intercalated dodecane and dodecanol (Figure 6b) at the clathrate–dodecane interface, because both expose a dense forest of alkyl tails to the water droplet. Our prediction that the dodecanol monolayer makes the clathrate–dodecane surface super-hydrophobic is consistent with the water wetting angles higher than 150$^\circ$ reported in experimental studies of the hydrate–cyclopentane interface in the presence of quaternary ammonium AA.\textsuperscript{37}

We note that if the dodecanol-covered clathrate is exposed to vapor instead of alkane, the contact angle decreases from 180$^\circ$ to 88 $\pm$ 2\textsuperscript{o} (Figure 6c), because the van der Waals interactions between water and alkane stabilize the water droplet more than vapor does. The contact angle of a water droplet is the same for dodecanol- or hexanol-covered clathrates. Interestingly, we find that even partial coverage of the clathrate surface by surfactants results in high contact angles for a water droplet. Our simulations indicate that if the surfactants are uniformly distributed on the clathrate surface with a density of about one surfactant per interfacial large cage (surface density 2.87 nm\textsuperscript{-2}), corresponding to 54\% coverage), the contact angle of a liquid droplet at the clathrate–vapor surface is $\sim$80$^\circ$. Such a uniform distribution of one adsorbed molecule per exposed clathrate half-cage may be expected if alkanes are present in the water phase, as they have very low solubility in water and will strongly adsorb to the clathrate–water interface by one of their methyl ends, exposing the other to water.\textsuperscript{68} We conjecture that the unexpectedly high $\theta = 94.2 \pm 8.5\textsuperscript{o}$ water wetting angle on cyclopentane hydrate recently measured with micromechanical force apparatus\textsuperscript{57} could be due to the presence of longer-chain alkane impurities in the cyclopentane gas, as long chain alkanes have low solubility in water but are strongly attracted to the water–clathrate interface.\textsuperscript{68}

The surfactant-covered clathrate is, as expected, oil-wet (Figure 6d). The simulations concur with the experiments that the presence of a surfactant monolayer at the clathrate–oil interface changes the wettablility of the clathrate surface from water-wet to oil-wet by altering the hydrophobicity of the hydrate surface.

In summary, our analysis indicates that the surfactants do not make the coalescence of a bare water droplet and a surfactant-covered clathrate thermodynamically unfavorable; their role is to increase the kinetic barrier for that process. In next section we support this conclusion with molecular simulations.

**E. Surfactant Monolayers Provide a Kinetic Barrier for the Coalescence of Hydrate Particles and Water Droplets.** We now focus on the process of permeation of water through the surfactant monolayer and coalescence with the clathrate surface. The passage of water requires the opening of a gap in the surfactant layer. This can be achieved in two ways: through desorption of the surfactants into the alkane phase and through lateral density fluctuations in the monolayer. We expect that the coupling of these two modes is responsible for the rare creation of transient holes that allow water permeation.

As the formation of a channel in the dodecanol monolayers is a rare event, we here investigate the molecular process of water penetration and coalescence by preparing model systems with openings of different sizes in the monolayer, which we create by removing dodecanol molecules in contact with the
water droplet. We perform these simulations for the clathrate—surfactant—vapor interface, because the clathrate—surfactant—oil interface is so hydrophobic that there is virtually no contact between water and the surfactant layer in the time scales of our simulations. We create an opening by removing a cluster of \( M \) neighboring surfactants from the monolayer. We note that the surfactants in the monolayer are allowed to move freely after the void has been created. Hence, water has to fill the pore before it closes. We find that the creation of a channel with area \( 72 \, \text{Å}^2 \) by removal of a cluster of \( M = 4 \) surfactants is sufficient for the water droplet on top of the monolayer to reach the clathrate surface within 5 ns. We perform simulations of water penetration with droplets of pure water and of water that contains 1 methane every 17 water molecules, well above the solubility of methane in liquid water. The latter case was chosen to promote the growth of clathrate after the droplet penetrates the monolayer. We find that the dynamics of water penetration is not affected by the presence of methane. The fast transfer of the water droplet through the opening evinces a large thermodynamic driving force, mostly driven by the difference in the cost of the water—vapor (or water—oil) interface and the water—clathrate interface, as illustrated in Figure 1. As the solubility of methane in water is always lower than in the clathrate crystal, the growth of the crystal upon penetration of the droplet will be subjected to additional barriers due to the slow penetration of methane through the interfacial layer, which have been computed in ref 39. Interestingly, we find that the penetration of water through the surfactant leads to the development of local curvature at the interface that strains the surfactant barrier, and should result in an accelerated rate of accretion with new incoming water droplets.

The kinetic barrier that impedes the coalescence and the agglomeration process is controlled by the free energy of adsorption of the surfactants to the clathrate surface and their mobility at the interface. The free energy barrier to desorb a single dodecanol molecule from the clathrate—dodecane interface is \( \sim 9 \, \text{kcal mol}^{-1} \) (Figure 2), which corresponds to desorption of a surfactant every \( \sim 1 \, \mu \text{s} \). Quaternary ammonium AAs bind stronger to the surface, providing higher stability against density fluctuations of the monolayer. We expect that the more compact monolayer results in larger desorption barriers and rarer lateral density fluctuations in the monolayer that can create an opening for water to reach the hydrate.

In the dense monolayers that intercalate dodecane and dodecanol, the alkane molecules exchange faster than the surfactants, as discussed in section 3C. We find that about a third of the alkane molecules in the compact monolayer with about 50% dodecanol and 50% dodecane exchange with the bulk alkane within 200 ns (throughout which none of the surfactants detach from the surface, consistent with the desorption times estimated above). The departing alkane molecules, however, are replaced by dodecane molecules from the oil phase within \( \sim 2 \, \text{ns} \). Although these individual exchanges do not produce large openings for the penetration of water, they modulate the density of the monolayer and would increase the probability of creation of a gap that nucleates the coalescence of hydrate and droplet. This suggests that mixed alkane-surfactant monolayers would provide lower barriers for water penetration compared to an equally dense pure surfactant monolayer, despite having essentially the same contact angle for a water droplet.

In section 3C we show that hexanol does not intercalate alkanes, irrespective of whether these are short (hexane) or long (dodecane). Compact hexanol monolayers may be achieved at high density of surfactants in the oil phase. Nevertheless, experiments indicate that hexanol monolayers do not become compact and crystalline at temperatures relevant to oil and gas pipelines. Moreover, the “hydrophobic channel” that water has to bridge to reach the hydrate is very short for hexanol and other similarly short-chain surfactants, increasing the likelihood of water permeation. Indeed, our simulations indicate that water permeates the hexanol monolayer within nanoseconds, although its surface density, 5.1 nm\(^{-2}\), and contact angle (see section 3D) are the same as for the pure and intercalated dodecanol monolayers that do not allow permeation in the 200 ns we evolve the simulations. Our analysis explains why short surfactants are not effective AAs, and reveals that the contact angle alone is not sufficient predictor of the ability of the monolayer to act as a barrier.

We conclude that the presence of a compact interfacial layer at the clathrate interface not only creates a hydrophobic surface that repels the water droplets, minimizing their contact with the surfactant-covered clathrate surface, but also gives rise to a kinetic barrier for the penetration of water to the crystal surface. The accretion of a bare water droplet and a surfactant-covered clathrate is favored by thermodynamics but delayed by the free energy barrier associated with the formation of an opening that allows for the transport of water to the clathrate surface. If both clathrate and water droplets are covered with surfactants, the driving force for coalescence of water and clathrate will diminish, and the barrier for the penetration of water to the clathrate surface will increase.

4. CONCLUSIONS

In this work we use molecular dynamic simulations to determine the effect of surfactants on the wettability of the clathrate interface by water and oil, characterize the process of...
coalescence of water droplets with clathrate hydrates covered with various alkanol surfactants, and elucidate the roles of the structure of the surfactant monolayer and the dynamics and strength of binding of the surfactants to the clathrate—oil interface on the performance of surfactants as AAs.

We find that alkanols bind equally strongly to the clathrate—water 68 and clathrate—alkane interfaces. The mode of binding, however, is quite different. Amphiphiles bind to the clathrate—water interface by adsorbing their alkyl end to empty half-cages at the clathrate surface, driven by the entropy of dehydration of the alkyl groups. 68,83,92,103 On the other hand, binding of water interface by adsorbing their alkyl end to empty half-cages of water 68 and clathrate − covered clathrate − agree with experimental reports. 37 We expect that the binding of charged surfactants to the clathrate − oil interface will also be driven by their enthalpy of transfer from the oil to the aqueous clathrate surface. The larger enthalpy involved in the hydration of charged groups explains why the free energy of adsorption of charged surfactants is up to four times larger 83 than here found for the alkanols. We expect that charged surfactants, because they are more strongly bound to the clathrate—oil interface, would result in less fluctuations in the density of the interfacial film, and higher barriers for the formation of gaps in the monolayer that allow for the penetration of water that leads to agglomeration.

The diffusion of individual surfactants at the clathrate—water and clathrate—oil interfaces also shows significant differences. The diffusion of dodecanol is hindered at the clathrate—water interface due to the deep adsorption of the methyl groups into the open half-cages at the clathrate surface. On the other hand, dodecanol molecules are highly mobile at the clathrate—alkane interface despite its strong binding, because the surfactant grazes the surface by moving between adjacent hydrogen bonding sites. The high mobility of the surfactant molecules at the clathrate—oil interface, together with their ability to bind to any hydrogen bonding site at the clathrate surface, allows for the formation of strongly bound dense surfactant monolayers at the clathrate—alkane interface. These dense monolayers provide a kinetic barrier that makes the clathrate surface resistant to water.

The formation of a compact interfacial film is key to provide a large enough barrier to prevent the merging of a water droplet and a clathrate particle. We find that alkanols and alkanes with similar and long- enough alkyl chains, e.g., dodecanol in dodecane, form dense mixed interfacial films already with less than 50% surface coverage of surfactant. Mixing between alkanes and surfactants in the monolayer is key for the alignment of the interfacial alkanes and the formation of compact smectic-like monolayers with orientational, but not positional, order. The simulations indicate that mixed aligned monolayers cannot be achieved with short alkyl chains, e.g. hexanol in hexane. Our results for the alkanols at clathrate—alkane interfaces are in agreement with previous reports for ionomic surfactants at the water—alkane interface in experiments 34,42 and at the clathrate—alkane interface in simulations. 38 We conclude that the formation of an ordered interfacial film depends on the length of the surfactant and alkane, but not on whether the surfactant is neutral or ionic.

It has been proposed that increasing the water contact angle on surfactant-covered clathrate hydrates leads to a significant reduction of the agglomeration of the clathrate particles with water droplets. 37 The simulations indicate that surfactant-covered clathrate—oil interfaces are super-hydrophobic, in agreement with experimental reports. 37 We find that a high contact angle is not sufficient to prevent the agglomeration of water and clathrate. For example, the contact angle of water on a hexanol-covered clathrate surface is almost the same as for a dodecanol-covered surface. Nevertheless, the hexanol film is not as dense nor aligned as the dodecanol one, and it allows for the fast penetration of water through the monolayer, leading to the growth and agglomeration of hydrates. The simulations suggest that the chain length and density of the surfactant are equally or more important than the contact angle in preventing the agglomeration of clathrate hydrates.

Our analysis indicates that a dense monolayer composed exclusively of surfactants will provide the highest barrier for water permeation, because surfactants are more strongly bound to the clathrate surface than alkanes. Hence, surfactants are less likely to desorb from the surface than intercalated alkanes in a mixed monolayer, resulting in fewer defects that would allow for water permeation. Short-chain surfactants, however, form films that are not compact and cannot intercalate alkanes. These films are easier to trespass than those formed by long chain molecules. We conclude that short chain surfactants are not viable to prevent the agglomeration of clathrate hydrates, even if the oil phase is composed of short alkanes.

In summary, this study presents a molecular perspective of the factors that control the wetting and agglomeration of clathrate hydrates and presents principles for the molecular engineering of effective antiagglomerants that would form a compact interfacial film impeding the coalescence of water droplets and hydrate particles.

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