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Influence of Surfactants on Sodium Chloride Crystallization in Confinement

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ABSTRACT: We study the influence of different surfactants on NaCl crystallization during evaporation of aqueous salt solutions. We found that at concentrations of sodium chloride close to saturation, only the cationic surfactant CTAB and the nonionic surfactant Tween 80 remain stable. For the nonionic surfactant, the high concentration of salt does not significantly change either the critical micellar concentration (CMC) or the surface tension at the CMC; for the cationic surfactant, the CMC is reduced by roughly 2 orders of magnitude upon adding the salt. The presence of both types of surfactants in the salt solution delays the crystallization of sodium chloride with evaporation. This, in turn, leads to high supersaturation which induces the rapid precipitation of a hopper crystal in the bulk. The crystallization inhibitor role of these surfactants is shown to be mainly due to the passivation of nucleation sites at both liquid/air and solid/liquid interfaces rather than a change in the evaporation rate which is found not to be affected by the presence of the surfactants. The adsorption of surfactants at the liquid/air interface prevents the crystallization at this location which is generally the place where the precipitation of sodium chloride is observed. Moreover, sum frequency generation spectroscopy measurements show that the surfactants are also present at the solid/liquid interface. The incorporation of the surfactants into the salt crystals is investigated using a novel, but simple, method based on surface tension measurements. Our results show that the nonionic surfactant Tween 80 is incorporated in the NaCl crystals but the cationic surfactant CTAB is not. Taken together, these results therefore allow us to establish the effect of the presence of surfactants on sodium chloride crystallization.
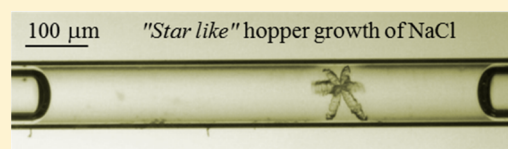
INTRODUCTION

Sodium chloride (NaCl) is the most abundant salt on earth and its crystallization is a key factor in many processes. Apart from its essential role in the food industry, it is one of the key components for paper and soda ash production. Sodium chloride is also commonly used in oil well drilling and is the primary deicing compound on roads during winter with an average use of 10 million tons per year in the United States and 1 million tons per year in France.[1] For most of the applications, the salt has to be transported from production to storage locations. Because of the hygroscopic properties of the salt and with environmental fluctuations of temperature and relative humidity, the salt grains have the tendency to lump together. In order to prevent this, additives known as anticaking agents, mostly ferrocyanides, are added to the salt in order to prevent crystals from growing together and agglomerating.[2,3] There is still a large research effort going into the development of new anticaking agents that do not pose any risk to the environment and our health.

Deicing salts on the roads inevitably end up dissolving in water when the snow and ice melt, and by capillary action invade the groundwater and subsequently end up in civil engineering structures (i.e., bridges and buildings) and outdoor artworks. Their presence there can produce damage; both mass loss and weakening have been reported.[4−9] As an example, chloride corrosion is a major issue for bridges; the salt solution which penetrates through existing cracks in the concrete can induce the corrosion of the steel that is used for the reinforcement.[8,9] Subsequently, the expansive forces produced from the corroded steel will induce the spalling of the concrete. Furthermore, with temperature and relative humidity fluctuations, through evaporation of the water, the dissolved salt can again crystallize in the porous materials. Direct consequences of crystallization in such porous media are the reduction of the permeability,[10,11] a major problem in oil recovery and soil mechanics, and the weathering of the mechanical and physical properties of civil engineering structures and artworks.[5−7] It has been reported that salt crystallization in the porous network (i.e., confinement) can lead to the development of a "crystallization pressure" exerted by the growing crystal onto the pore walls, that eventually causes disintegration of the stones.[7,12−14] In order to mitigate this problem, various strategies have been proposed. A strategy that has received considerable attention is again the use of additives that alter the crystallization phenomenon in such a way that it may prevent the development of the crystallization pressure.[15−18] Among these, surfactant molecules are an important class of additives that can modify the crystal growth process when present at very small concentrations, by adsorbing preferentially onto different crystalline faces. Surfactants or amphiphilic compounds are

Table 1. Behavior of Different Surfactants on High NaCl Concentration (5.5 m)

surfactant	type	CMC	ternary solution in 5.5 m NaCl
Cetyltrimethylammonium bromide (CTAB)-$C_{19}H_{42}BrN$	Cationic	0.8−1 mM[39]	**Transparent**
Cetyltrimethylammonium chloride (CTAC)-$C_{19}H_{42}ClN$	Cationic	1.3−1.7 mM[39]	**Transparent**
Sodium Dodecyl Sulfate (SDS)−$CH_3(CH_2)_{11}OSO_3Na$	Anionic	8−10 mM[40−42]	Precipitation
Ammonium Dodecyl Sulfate (ADS)-$C_{12}H_{29}NO_4S$	Anionic	6−8 m[43]	Precipitation
Sodium Dodecylbenzenesulfonate(SDBS)-$C_{18}H_{29}NaO_3S$	Anionic	1.4−1.6 mM[40]	Precipitation
Dioctyl sulfosuccinate (AOT)-$C_{20}H_{37}NaO_7S$	Anionic	2−6 mM[44]	Precipitation
Tween 80-$C_{64}H_{124}O_{26}$	Nonionic	1.5−15 μM[42]	**Transparent**
Triton-X-100-$C_{14}H_{22}O(C_2H_4O)_n$ (n = 9−10)	Nonionic	0.2−0.3 mM[40−42]	Precipitation
Silwet L-77-$C_{13}H_{34}O_4Si_3$	Nonionic	0.23 mM[45]	Precipitation

composed of a hydrophilic (polar) head and a hydrophobic (nonpolar) hydrocarbon chain. This configuration enables them to adsorb at the interface between two immiscible liquids such as oil/water and water/air. Surfactants can also adsorb at solid−liquid interfaces and may even adsorb differently on different crystal facets, which has a significant influence on crystal nucleation and growth.[19−23] Most studies report that the presence of surfactants inhibits crystallization, but there are also known exceptions in which to the contrary they increase the nucleation rate. For instance, the presence of sodium dodecyl sulfate was observed to increase the nucleation rate of $MgSO_4$.[24] These contradictory examples suggest that the crystal−impurity interactions are highly specific and need to be treated individually.[25,26] Even after numerous studies, no conclusive theory has been developed to predict the influence of surfactants on salt nucleation that allows one to tailor the surfactants for achieving specific effects on the formation of salt crystals.

In this paper, we study the influence of different surfactant additives on NaCl crystallization in confinement during evaporation of the ternary solutions. To be able to discuss these issues, we first need to consider the counter-effect of high salt concentrations on the properties of surfactant solutions themselves. Usually, the properties of ionic (charged) surfactants are tuned by adding small amounts of salt; in our case, however, we deal with very concentrated salt solutions close to the solubility limit of the salts for which not a lot of data can be found in the literature. We find that only cationic and nonionic surfactants are stable in solution at these high electrolyte concentrations. The presence of these surfactants is subsequently shown to inhibit the precipitation of the salt. This, in turn, leads to high supersaturation, which changes the dynamics of crystal growth. Another important finding is that the evaporation of water from the salt and surfactant solutions is not influenced by the presence of surfactants, contrary to what is sometimes claimed in the literature.[27−29]

■ EXPERIMENTAL SECTION

Effect of High Salt Concentration on Surfactant Properties. Low concentrations of soluble salts are commonly used to tailor surfactants properties such as the critical micellar concentration (CMC), the aggregation number in the micelles, and the equilibrium surface tension.[30−35] Also in our system, there is one surfactant plus a salt. The presence of the latter can alter the electrostatic repulsion between the headgroups (for charged surfactants) and the Debye layer around the micelles, leading to changes in micelle size and shape.[35] This of course also changes the adsorption and surface tension. However, there is only a limited number of studies on micelle formation at concentrations of sodium chloride close to saturation, which is relevant for crystallization.[36,37] These studies also discuss the miscibility of salts within the surfactant micelles and the adsorbed films

in order to assess the modified characteristics of micellar systems by the addition of salt.[37] In principle, the thermodynamic analysis of the surfactant behavior in the presence of salts can also be used to deduce any possible change in the composition of micelles,[38] but this is beyond the scope of the present paper, which focuses on the effect of surfactants on the crystallization of the salt.

In order to choose our surfactants for the crystallization experiments, we first tested different type of surfactants: cationic, anionic, and nonionic for their solution stability (Table 1). Ternary solutions of NaCl and surfactant in water are prepared by first preparing surfactant solutions at their critical micellar concentration (CMC) followed by adding NaCl (Sigma-Aldrich purity ≥99%) to a concentration of 5.5 m (molal or mol/kg of water) which is slightly below the saturation concentration (C_s = 6.14 m). All the anionic surfactants precipitated upon the addition of salt; the cationic surfactants CTAB and CTAC remain stable and form transparent solutions. The origin of this interesting asymmetry between cationic and anionic surfactants is unclear. Among the nonionic surfactants, Tween 80 is the only one that remains stable in the presence of high NaCl concentration. The sensitivity to the salt concentration is found to be different for the anionic and nonionic surfactants. For example, the threshold concentration for the anionic one, SDS, is around 0.5 m of NaCl, whereas the nonionic surfactant Triton-X-100 can stay stable up to 4 m of salt; precipitation is observed rapidly above these concentrations.

Consequently, for the crystallization experiments in the presence of surfactants only CTAB (Sigma-Aldrich purity ≥99%) and Tween 80 (Ameresco, proteomics grade purity) which make transparent ternary solutions were chosen (Figure 1). The physicochemical properties of CTAB and Tween 80 (Figure 2) solutions were characterized prior to the crystallization experiments.

The surfactant adsorption at the liquid/air interface was characterized by measuring the surface tension γ_{lv} and the CMC of the ternary solutions using a Kruss K100 tensiometer based on the Du
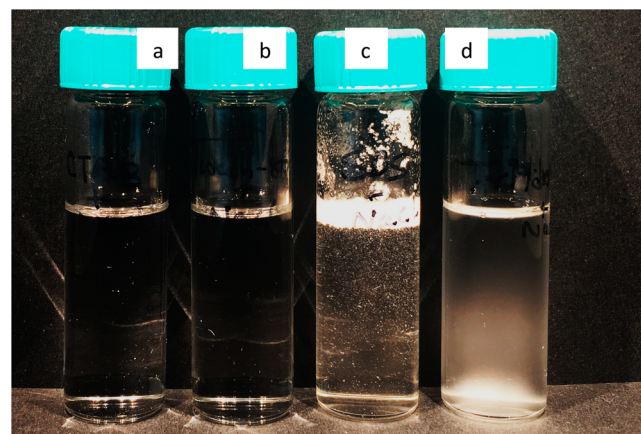

Figure 1. Surfactants after addition of 5.5 m NaCl. The transparent solutions of (a) CTAB and (b) Tween 80 and precipitation with (c) SDS and (d) Triton-X-100.
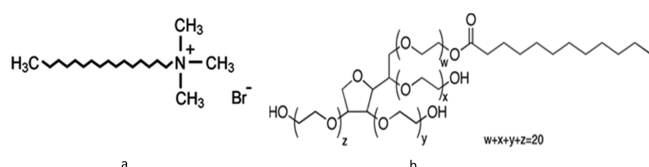
Figure 2. Molecular structure of (a) CTAB and (b) Tween 80.

Noüy ring method. The latter is based on measuring the force to slowly raise a platinum ring, dipped in the liquid, from the liquid's surface. The surface tension is then calculated from the diameter of the ring and the tear-off force. The results as a function of the concentration were obtained by performing automatic dilutions; we start at high surfactant concentration at 5.5 m NaCl and dilute with salt solution at 5.5 m. In this way, the instrument allows us to measure the surface tension values for very small concentration steps of the surfactant. As far as equilibration of the solutions is concerned, for each dilution step, the solution is stirred for 30 s, and the value of the measured SFT is registered only when the standard deviation between five consecutive measurements is within 0.1 mN/m. Consequently, the average total time taken for one measurement is around 10 min (depending upon how fast the system equilibrates) which is normally long enough for the equilibration of most the surfactants.

The adsorption at the solid/liquid interface of glass of both surfactants in the salt solution was studied by performing sum frequency generation (SFG) experiments. We have probed the CH vibrations of the surfactants and the OH vibrations of the water molecules at the solid interface. In this method,[46] a broadband infrared laser beam exciting molecular vibrations and a narrowband near visible laser beam are overlapped in space and time at the interface. The resulting sum-frequency signal is strongly enhanced if the infrared is resonant with a molecular vibration. Because of its selection rules, this process is forbidden in centrosymmetric media, like bulk water, therefore giving the IR spectrum of only interfacial molecules. The signal intensity is a measure of the amount of order present at the interface.

Salt Nucleation and Growth Experiments in the Presence of Surfactants. The primary nucleation and growth of NaCl crystals was studied in confined geometry by controlled evaporation of aqueous solutions under the microscope. The schematic of the setup is shown in Figure 3. The concentrations of CTAB and Tween 80 used were 9×10^{-4} m and 7.6×10^{-5} m, respectively, both of which are above their respective CMCs and the NaCl concentration used was 5.5 m which is slightly below the saturation concentration. In order to observe the influence of surfactants on crystallization, the results are compared with the evaporation and crystallization of pure NaCl solution at 5.5 m.
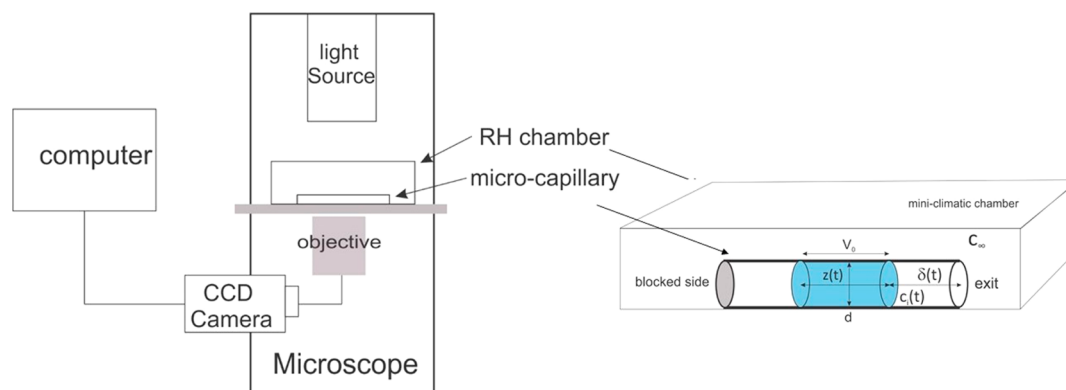
A small volume of salt solutions with and without surfactants were introduced by capillary action in cylindrical borosilicate glass microcapillaries (Vitrocom, $d = 100$ μm). After closing one of the sides of the microcapillary using epoxy glue, the capillary was placed in a controlled miniclimatic chamber held at a constant relative humidity (RH = 55 ± 2%) and room temperature ($T = 22 ± 1$ °C).[47] This whole construction is placed under a Leica DM IRM inverted microscope and the subsequent displacement of the meniscus resulting from evaporation is followed with 5× and 10× magnification objectives from which the change in volume is calculated by analyzing the images taken by a CCD camera. The latter has a resolution of 800 × 600 pixels and a 8-bit sensitivity; the time interval between the images was set to 5 s. The volume variation also allows us to determine the evolution of the concentration and calculate the supersaturation of the solution prior to crystallization. Once crystallization happens, the shape of the crystal and its growth rate are followed during each experiment.

■ RESULTS AND DISCUSSION

Effect of High NaCl Concentration on the Physicochemical Properties of CTAB and Tween 80 Solutions. We have measured the surface tension of CTAB and Tween 80 solutions as a function of concentration of the surfactants in the absence and presence of NaCl in the solution (Figure 4). Two salt concentrations were used: a relatively small concentration 0.01 m and a high salt concentration 5.5 m; the latter is used subsequently as the initial concentration in the crystallization experiments. The CMC values obtained for CTAB in water and in brine solution at 0.01 m are seen to be in good agreement with the literature data;[48,49] the addition of NaCl to the CTAB solution drastically shifts the CMC of CTAB from $\sim 9 \times 10^{-4}$ m without salt to $\sim 2 \times 10^{-5}$ m at high NaCl concentration (5.5 m). In addition to the decrease of the CMC, another important observation here was that the equilibrium surface tension after the CMC was seen to be lower $\gamma_{CMC} \sim 32$ mN/m at 5.5 m NaCl compared to that of the pure solution of CTAB without salt ($\gamma_{CMC} \sim 37$ mN/m). Interestingly, the slope below the CMC tells us (using the Gibbs adsorption equation) that without salt, there is more CTAB present on the interface. The lower surface tension at the CMC that is observed when salt is added must then be due to the change in chemical potential of the surfactant molecules in the bulk due to the presence of salt.

In the case of nonionic surfactants also, studies have reported that the addition of electrolytes decreases the CMC value,[50] but surprisingly, for the case of Tween 80, we do not observe a

Figure 3. Schematic of the experimental setup used for following the evaporation of ternary solutions (initial volume V_0) and the crystallization in microcapillary ($d = 100$ μm). c_∞ is the controlled water vapor concentration of the climatic chamber and $c_i(t)$ the water vapor concentration just above the meniscus at time t; $\delta(t)$ is the distance over which water vapor diffusion takes place during the evaporation from the open side of the capillary.
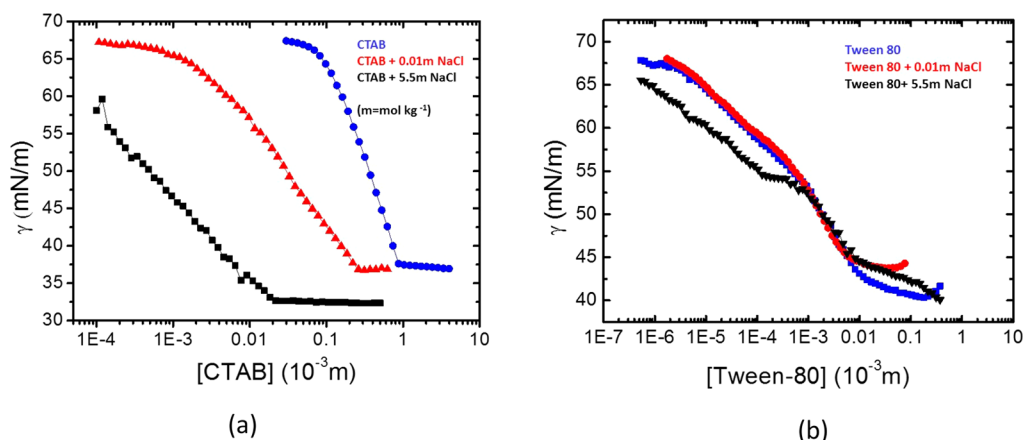
Figure 4. Surface tension as a function of (a) CTAB and (b) Tween 80 in water and salt solutions at different concentrations.

significant change in the CMC (1.5×10^{-5} m) even in the presence of very high salt concentrations. Also unlike the case of CTAB, there is no observable change of the surface tension at the CMC upon the addition of salt, $\gamma_{lv\text{-CMC}} \sim 42$ mN/m.

The different behavior of ionic and nonionic surfactants in terms of decrease in CMC can be attributed to the fact that addition of salts in ionic surfactants decreases the electrostatic repulsion between the head groups, thereby favoring their aggregation.[35] However, in the case of the nonionic surfactant Tween 80, the repulsion between the head groups is not a limiting factor for micellization, which is the reason we do not see any change in CMC upon addition of salt.

Therefore, we start our crystallization experiments with ternary solutions of CTAB and Tween 80 that have similar CMC, whereas without salt the CMC of the ionic surfactant is much higher.

Effect of Surfactants on NaCl Crystallization. For the crystallization experiments, the volume change during the evaporation of the solutions inside the microcapillaries is subsequently followed by recording the displacement of the meniscus while simultaneously visualizing the onset of crystal growth in the solution directly under the microscope coupled to a CCD camera. In this way, the evolution of the concentration with the evaporation up to the crystallization point can be determined (Figure 5).

The first important parameter examined to account for the influence of surfactants on the crystallization is the super-saturation, $S = c/c_s$, at which nucleation takes place (Figure 5).
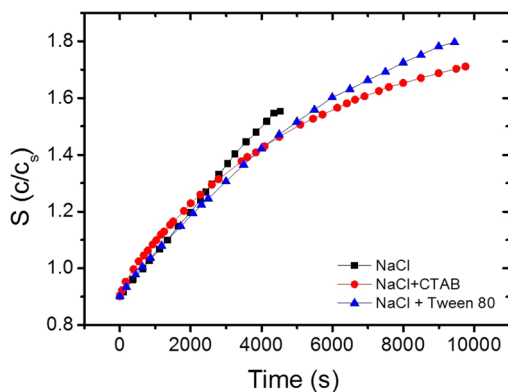

Figure 5. Evolution of the supersaturation of the solutions with evaporation until spontaneous crystallization.

The supersaturation is defined as the ratio of the concentration at the moment of crystallization c to the saturation concentration c_s (6.14 m); thus, the value of the supersaturation gives an indication whether the nucleation is inhibited or promoted compared to the crystallization of pure NaCl solution under the same experimental conditions. (Table 2)

Table 2. Mean Value of Supersaturation Achieved at the Onset of Crystallization for Pure NaCl and the Ternary NaCl−Surfactant Solutions

initial solution	supersaturation (c/c_s)
Pure NaCl Solution (5.5 m)	1.57 ± 0.1
NaCl (5.5 m) + CTAB (9×10^{-4} m)	1.72 ± 0.02
NaCl (5.5m) + Tween 80 (7.6×10^{-5} m)	1.78 ± 0.01

summarizes the mean value of the supersaturation obtained over ∼20 experiments for each solution. For a pure sodium chloride solution, the supersaturation at which the spontaneous nucleation and growth occurs was found to be $S = 1.57 \pm 0.1$, in agreement with earlier experiments.[51] In the presence of CTAB and Tween 80, reproducibly higher supersaturations are reached (Table 2). Moreover, in the presence of surfactants, the variability in the supersaturation in different experiments becomes smaller. The increase of the supersaturation in the presence of surfactants suggests that the crystallization is inhibited by both CTAB as well as Tween 80 in the solution. These very high supersaturations lead to a rapid growth of the crystal which favors the formation of only a single crystal in small volume (both with and without surfactant) with a peculiar hoppered (skeletal) shape[51] (Figure 6a). The hopper growth is only observed at early times in the growth process; at later times due to the rapid decrease of the local supersaturation, the extremities of the hopper crystal will continue a slower growth as a cubic crystal eating up the smaller cubes attached to it.[51]

Another important observation here is that in the presence of surfactants the nucleation happens in the bulk of the solution, in contrast to the pure NaCl solution where the growth of the crystal takes place mostly at the liquid−air interface in evaporation experiments (Figure 6).[51−54] This can explain the higher supersaturation reached when surfactants are added; the nucleation at the interface is heterogeneous, and the energy barrier for heterogeneous nucleation near a surface is smaller than that for homogeneous nucleation. In general, nucleation is easier in contact with a surface; because of geometrical reasons the size of the critical nucleus is smaller.[55] This reduction in

Figure 6. First appearance of crystals (5 s time-window) in (a) pure NaCl solutions, (b) the multibranched hopper formed in the NaCl solution with CTAB, and (c) the solution with Tween 80; when the hopper crystal grows rapidly and reaches the wall of the capillary, a change in the direction of the branches can be seen. (d,e) Illustration of hopper crystal with one branch and (e) star-like hopper crystal (multibranched) formed in bulk in the presence of CTAB and Tween 80.

surface area of the nucleus reduces the height of the energy barrier that needs to be overcome in order to form the surface of the growing nucleus.[56−58] The main action of the surfactant is then to passivate this liquid−air interface, i.e., passivation of this interface when surfactants are present leads to a higher supersaturation before nucleation to takes place.

To show that the surfactants also passivate the solid−liquid interface, sum frequency generation (SFG) experiments were performed. Figure 7 shows SFG spectra for the glass surface in
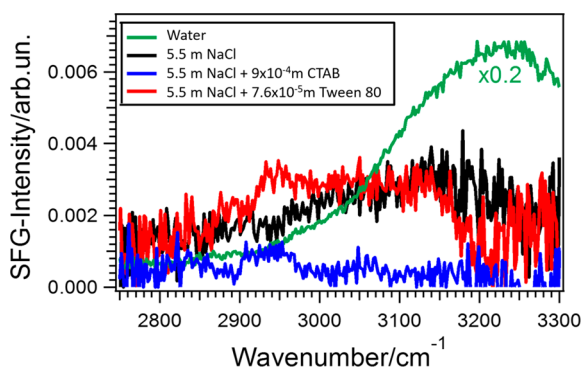

Figure 7. SFG spectra for different salt solutions in contact with a glass (SiO$_2$) window. The water curve has been multiplied by 0.2 to make the intensity comparable to that of the other curves.

contact with different salt solutions with and without surfactants. For the case of water and the pure salt solution there is no CH vibration visible in the range between 2800 and 3000 cm^{-1}. Between 3000 and 3300 cm^{-1} the broad water band is visible. The water signal is very low for the salt case, because the salt screens the negatively charged SiO$_2$ surface and thereby reduces the order of the water molecules and thus the SFG signal. In the cases of Tween 80 + NaCl and CTAB + NaCl, weak but clear peaks are visible in the range of 2900 to 2970 cm^{-1}. This is a clear indication that both the nonionic Tween 80 as well as the cationic CTAB are present at the solid surface.

Moreover, our results show that surfactant molecules or micelles in the solution do not act as nucleation sites in these experiments. If this was really the case, it should make nucleation more favorable, and consequently spontaneous precipitation and growth should be seen at lower super-

saturation compared to pure NaCl. We observe, to the contrary, that with surfactants the nucleation is rather inhibited (higher supersaturation are reached prior to nucleation).

The nucleation at a higher supersaturation results in the observed multiple branched "star-like" hopper crystals because of the precipitation of new cubic crystals on the edge of the pre-existing cubic nucleus in the bulk. Because the rapid growth of the hopper crystal is unchanged in the presence of Tween −80 and CTAB, their adsorption to the supercritical nuclei limiting the growth is excluded by our observations.

It is well-known that in salt solutions the evaporation rate could be another key factor determining the supersaturation at which nucleation takes place.[51,56,59] If the nucleation happens at the liquid meniscus, such as for the pure NaCl solution, it could be that the local supersaturation is higher in this region as the evaporation takes place at the liquid/air interface. If the evaporation is faster than the ion transport in the solution, a concentration gradient can develop close to the meniscus with a higher local concentration that can lead to an increase of the nucleation rate.

We therefore examine the influence of CTAB and Tween 80 on the evaporation rate of NaCl solution. It has been suggested by some authors that surfactants, by virtue of their partitioning at the interface, can block the evaporative surface, thereby leading to slower evaporation rates in cases of droplets, microcapillaries, as well as flat surfaces.[27−29,60,61]

The variation in volume of the solution in the cylindrical capillary is followed throughout the evaporation process; the evaporation rate dV/dt (m^3/s) is shown in Figure 8. For all cases, a decrease in the evaporation in time is observed. However, no change is observed in the evaporation rate when CTAB surfactant is added to water and to the salt solution. This is in fact not so surprising if one notes that in general for the evaporation of water the diffusion of water molecules through the vapor is the rate-limiting step:[51,62−64]

$$e \approx \rho_g D \frac{(c_i - c_\infty)}{\delta} \tag{1}$$

where e is the evaporation flux density; ρ_g the vapor density; D the diffusion coefficient of water vapor through the gas; c_∞ the controlled water vapor concentration of the climatic chamber (55%) and c_i the water vapor concentration just above the
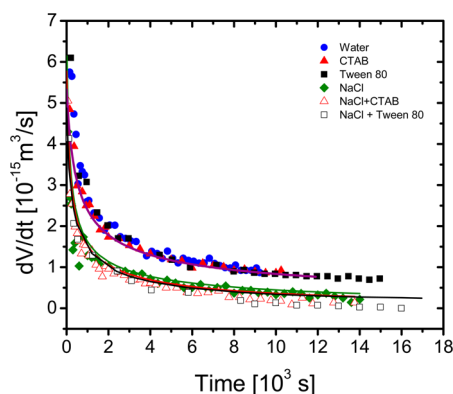
Figure 8. Microcapillary experiments (at $T = 21$ °C, RH = 55% ± 2): evolution of the evaporation rate for water and brine with and without surfactants (CTAB and Tween 80). The continuous line corresponds to the model based on diffusive transport (eq 2). The surfactant has no impact on the evaporation rate. The slight differences are mainly due to slight fluctuations of the experimental conditions in different microcapillaries (notably the distance between the meniscus and the outlet of the capillary and the relative humidity (±2%).

meniscus; δ is the distance over which diffusion takes place (Figure 3). We conclude that the surfactants do not have any significant influence on the evaporation rate. It is clear from eq 1 and Figure 3 that the drying rate is controlled by δ and ($c_i - c_\infty$). For water, the equilibrium vapor pressure above the meniscus remains constant and only δ will change over time with the displacement of the meniscus. This is the only reason for the decrease of the evaporation rate in time in the case of water. However, for salt solutions, apart from increasing δ, the second reason responsible for the decrease in the evaporation rate is the increase of salt concentration in time, which also changes the equilibrium vapor pressure above the meniscus $c_i(t)$ and the density of the liquid $\rho_l(t)$. Subsequently, eq 2 written in terms of time gives

$$\frac{dV}{dt} = DA \frac{\rho_g}{\rho_l(t)} \frac{c_i(t) - c_\infty}{\sqrt{\frac{2\rho_g}{\rho_l(t)}(c_i(t) - c_\infty)t + \delta^2}} \tag{2}$$

where $\frac{dV}{dt}$ is the evaporation rate; ρ_g the density of the gas phase; ρ_l the density of liquid phase; D the diffusion coefficient

of water through the vapor; c_i the water vapor mass fraction above the interface; c_∞ the water vapor mass fraction outside the capillary; δ_0 the initial vapor diffusion distance of meniscus; A the cross-sectional area πr^2 (r is the radius of the capillary). As can be seen in Figure 8, the model based on such diffusive transport describes the data very well, and for salt solution with and without surfactant, the decrease of the evaporation rate in time is therefore due to the effects of both δ and ($c_i - c_\infty$). Also, in agreement with this idea, the small characteristic dimension of our samples and the very slow evaporation rates ensures the homogeneity of solutions. Quantitatively, the heterogeneity in ion distribution in a solution can be inferred from the Peclet number, which is defined as the ratio of the convective and diffusive transport of ions in the solution. Since the Peclet number depends on the concentration of ions and the size of the system, in evaporating systems, it is time-dependent and changes as the evaporation progresses:

$$\text{Pe} = t_{\text{diff}}/t_s \tag{3}$$

where the diffusion time $t_{\text{diff}} = z^2/D_{\text{NaCl}}$ and the convection time $t_s = z/(dz/dt)$; z is the length of the solution cylinder at time t and D_{NaCl} is the diffusion coefficient.[64] For pure NaCl solution as well as with CTAB and Tween 80, the values of Peclet number were found to be on the order of 10^{-3} to 10^{-4} at the point of crystallization.

Finally, we have determined with a simple method whether besides their role as nucleation inhibitor the micelles are incorporated within the crystal structure of sodium chloride because of its rapid growth. It has been shown by AFM experiments that for calcite crystals, micelles can be entrapped during growth because they bind specifically to steps, enabling successive steps to close around them.[20,65] It is reported that such incorporation can even increase at higher growth rates because of the greater rate of step generation with increasing supersaturation.[66]

To see whether this is also the case in our experiments, we perform bulk evaporation experiments in the same evaporation conditions, to have a larger quantity of crystal than in the microcapillary experiments. In the bulk experiment, we observe the same trend: CTAB and Tween 80 inhibit the nucleation process; i.e., crystal precipitation occurs sooner in a pure salt solution. The CTAB/NaCl solution is the next one to crystallize and Tween 80 the final one. Subsequently, the
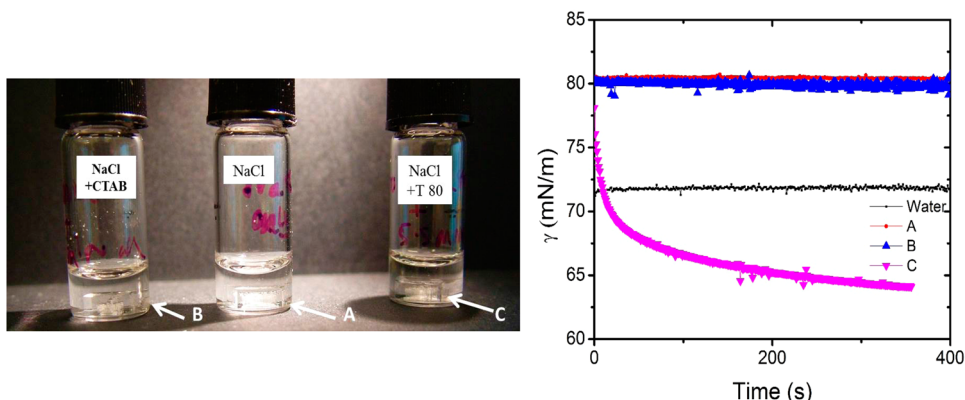

Figure 9. Dynamic surface tension measurements using pendant drop technique of salt solutions (5.5 m) made by the dissolution of crystals: A, B, and C in water. The precipitated crystals were collected, rinsed with saturated sodium chloride solution, weighed, and dissolved in water to obtain a solution at concentration of 5.5 m. The measurements were done at 75% relative humidity in order to avoid any evaporation process and concentration change, which could affect the value of the surface tension during the measurement time.

precipitated crystals (Figure 9) were collected, rinsed with a saturated sodium chloride solution, weighed, and dissolved in water to obtain NaCl solutions at concentration of 5.5 m. The rinsing with salt solution allows removal of physisorbed surfactant molecules from the crystal surface. The chemistry of the NaCl crystal surface and the functional groups at the hydrophilic head of the surfactant molecules makes it very unlikely for any chemisorption to take place. The pendant drop method employing a Kruss Easy-Drop instrument is used then to measure the surface tension of the resulting solutions obtained by the dissolution of the crystals. If surfactants are incorporated in the crystal, they will redissolve and lower the surface tension; if not, the surface tension will be that of the 5.5 m salt solution.

Our results show that the surface tension of salt solution made by the crystal collected from CTAB solution, within the experimental resolution, is identical to the surface tension of pure NaCl solution at 5.5 m (~80 mN/m) indicating the absence of any CTAB in the collected crystal. However, in the case of the solution made by the crystal collected from the Tween 80 solution, a lower surface tension of ~64 mN/m is measured which clearly reveals the presence of Tween 80 molecules in the solution after the dissolution of the crystal (Figure 9). The surface tension measurement by the pendant drop technique is therefore an easy way to obtain information on the interaction/incorporation of surfactants in salt crystals. In the context of crystallization damage, such incorporation can alter the mechanical properties of the crystallized salt. In the context of biomineralization, differences between different surfactants such as the one observed here can perhaps be useful to elucidate the conditions under which incorporation occurs.

CONCLUSION

In this paper, we present results on the evaporation of ternary solutions of surfactants and NaCl at high salt concentrations until crystallization occurred. The anionic surfactants tested in this study are found to be incompatible with highly concentrated NaCl solutions: they precipitate. On the other hand, the cationic surfactants CTAB (and CTAC) and the nonionic surfactant Tween 80 form homogeneous ternary solutions. The high electrolyte concentration reduces the CMC value and the surface tension at CMC of the cationic surfactant; no change is observed for the nonionic. Our results show that the evaporation rate is not affected by the presence of surfactants as the evaporation rate is controlled by diffusive transport through the gas phase.

The presence of both surfactants in the salt solution delay the crystal nucleation by a significant amount leading to a high supersaturation prior to precipitation during evaporation. This inhibitor role seems to be due to a passivation of nucleation sites, i.e., the availability of the liquid/air and solid/liquid interface. It follows from thermodynamic considerations that the free energy for the nucleation process mediated at a surface can be roughly half of that required to nucleate in the bulk,[55,57,58] which provides a plausible explanation for the higher supersaturations reached when nucleation at the solution/air or solid/liquid interface is prevented by the presence of surfactants there. The high supersaturation has the consequence that in the first seconds of precipitation the rapid growth of one "star-like" hopper crystal is observed in the solution. Because the nucleation occurs in the bulk, the higher the supersaturation is, the more branched the hopper crystal

appears. Even though the growth of the nucleus is very fast, the incorporation of surfactant micelles in the crystalline structure depends on the nature of the surfactant. Surface tension measurements have been used as a simple and accurate method to get information on the interaction/incorporation of surfactants in the crystalline structure. Our results show that the nonionic Tween 80 surfactant is incorporated in NaCl crystals. The cationic surfactant is not, which could be due to some electrostatic repulsion between the negatively charged surfaces of the NaCl crystal[12] and the cationic micelles surrounded by chlorine ions.

The incorporation of copolymer micelles in calcium carbonate crystals has been used as a simple model to understand biomineral formation; a mechanism of occlusion within single salt crystals has been proposed recently to describe this.[20,65] The results reported in this paper bring some new insights on the role of surfactants on the kinetics of salt precipitation at high electrolyte concentration and their interaction with the crystalline structure.

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Notes
The authors declare no competing financial interest.

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