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Multiscale Study on the Mechanism of a Bio-Based Anticaking Agent for NaCl Crystals

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ABSTRACT: Caking constitutes a major problem for the flowability, transport, packaging, and consumption of hygroscopic granular crystalline materials such as salt. Sodium chloride is the most abundant salt on the earth and known to form strong lumps, mainly due to cycles of water uptake and water evaporation. We report on a multiscale study of the anticaking effect of the bio-based additive Fe-mTA, a metal–organic complex of iron (III) and meso-tartrate. Drying-deliquescence cycling experiments are performed to reproduce the situation in which the salt undergoes repeated humidity fluctuations. Our results show that Fe-mTA acts as a nucleation promoter and growth inhibitor by inducing roughness on the surface of crystals. To directly study the effect of Fe-mTA down to the micrometer scale, we study liquid capillary bridges between two macroscopic salt crystals by applying droplets of salt solution with various levels of additives. Scanning electron microscopy and three-dimensional (3D) laser scanning confocal profilometry results show that Fe-mTA produces a surface roughness at the micron scale. This roughness decreases the effective contact area between crystals and promotes the spreading of the liquid bridge; consequently, the formation of a solid bridge between grains with water evaporation is avoided, thus preventing the caking phenomenon and, in addition, preventing adhesion of the crystals to solid substrates.

INTRODUCTION

Sodium chloride (NaCl), commonly known as salt, is an essential nutrient for life and one of the most abundant minerals on the earth. Once considered a luxury, salt is nowadays an ordinary material with a wide range of applications ranging from cooking to large-scale industrial use. Once produced, salt is stored and transported in different ways for various applications. For handling purposes, its flowability as a granular material is of major concern. However, salt is strongly subject to caking, a phenomenon where individual salt grains agglomerate together (Figure 1) and form big lumps of solid material. This phenomenon is due to the salt’s hygroscopic properties in combination with fluctuations in humidity and/or temperature of the environment. To prevent the caking phenomenon and to prevent crystals from agglomerating, additives known as anticaking agents are added to the salt.

For NaCl, the most widely used anticaking agent is based on ferrocyanide or [Fe(CN)₆]⁻⁴. The sodium salt in its hydrous form is also known as yellow prussiate of soda (YPS). To be effective, only 2.5 ppm (equivalent to 2.5 mg/kg) of YPS is required in salt. However, YPS has important drawbacks. In the chlorine-alkali industry, one of the most important industries using sodium chloride, YPS can enter the membrane electrolyzers and iron deposits as Fe(OH)₃ on or in the membranes and potentially affects the electrodes. Thus, it may lead to increased power consumption and a shortened lifetime of membranes and electrodes. Moreover, in electrolyzers, cyanide is (partially) transformed to the harmful derivative NCl₃ that may lead to explosions even at the ppm level in liquid chlorine. To avoid these disadvantages, a new type of bio-based anticaking agent has been developed based on tartrate derivatives originating.
from grapes processing for the wine industry. This additive is a complexation product between sodium tartrate (with its three stereoisomers, as shown in Figure 2) and iron (III) chloride.

![Figure 2. Stereoisomers of tartaric acid: (a) levo-tartaric acid (L-TA), (b) dextro-tartaric acid (D-TA), and (c) meso-tartaric acid (mTA).](image)

Since iron meso-tartrate is the key functional complex in the additive, the anticaking agent is called Fe-mTA or mTA. It has been shown to be quite effective even at low concentrations with an industrial dosing level of only 3 ppm by weight. It also shows clear advantages in the membrane electrolysis process. Before being shown to be quite effective even at low concentrations with an industrial dosing level of only 3 ppm by weight, it also shows clear advantages in the membrane electrolysis process. Before entering electrolyzers, the Fe-mTA complex falls apart. The iron precipitates as Fe(OH)₃, which is subsequently removed by means of filtration. Tartrate is converted into HCl and CO₂ in the electrolyzers and no chlorinated components are formed. In addition, Fe-mTA is also biodegradable and cyanide-free.

Previously, Bode et al. studied the anticaking mechanism of YPS and Fe-mTA at the molecular level and showed the dominant mechanism to be a step-pinning phenomenon, where a molecule of the additive blocks the monoatomic step growth on the surface, and in this way influences the surface morphology of the growing crystals at the atomic scale. Townsend et al. suggested a link between the phenomenon of salt creeping and anticaking. Creeping is the evaporation-driven extension of crystallites beyond the solution boundary of a liquid on a solid surface. It was concluded that the amplitude of creeping can be used as a good indication of the effectiveness of an anticaking agent. Although these studies offer important insights into the action of anticaking agents, they cannot fully explain the mechanism of anticaking itself at the macroscopic scale.

Here, we report on the mechanism of anticaking of sodium chloride using Fe-mTA, at a larger scale than molecular ones, by combining microscopic and macroscopic-scale experiments. We performed several drying-deliquescence cycles to simulate humidity fluctuations at the root of the caking phenomenon. On the microscale, the impact of the anticaking additive on the nucleation of sodium chloride was investigated via crystallization by evaporating microdroplets of salt solutions deposited on glass slides followed by multiple deliquescence-drying cycles. In addition, the impact of the additive as a growth promoter or inhibitor was determined by small-volume evaporation experiments in microcapillaries, where controlled precipitation of one (crystal) nucleus was studied. Finally, at the macroscopic scale, the mechanism of anticaking was determined by performing capillary bridge experiments between two macroscopic NaCl crystals.

### MATERIALS AND METHODS

Three types of salt solutions are used:

- Undersaturated pure NaCl solutions at a concentration of 5.9 molal;
- NaCl solutions (5.9 molal) with Fe-mTA at 80 ppm;
- NaCl solutions (5.9 molal) with Fe-mTA at 160 ppm.

The Fe-mTA dosage of 80 ppm in solutions corresponds to typical industrial dosing levels on the final salt product. Solutions were prepared using ultrapure Millipore water, NaCl salt of Pharmaceutical grade with a very low percentage of impurities (Sanal P, purity > 99.9%), and mTA solution, both products provided by Nouryon. The characteristics of the solutions are summarized in Table 1. The addition of the mTA at such low concentrations does not change the physicochemical properties of the salt solution at 5.9 molal. The surface tension, density, and contact angles on the glass slide and NaCl crystal are the same for 160 and 80 ppm to within the experimental accuracy.

Microscopic studies are done by evaporating aqueous salt solutions of known initial concentrations, as described in Table 1, either as droplets (initial droplet volume ~0.57 ± 0.08 μL) on cleaned Corning Glass slides or introduced into glass microcapillaries (500 μm in diameter). By fixing the temperature (T ~ 21 ± 2 °C) and controlling the relative humidity (RH) of the ambient air in the climatic chamber, the evaporation rate of the solution is controlled. The relative humidity in our mini-climatic chamber is fixed by introducing an airflow with a controlled partial water vapor pressure. This is created by first flowing the air through the water at a given temperature T₁ in a water bath thermostat (for drying experiments, around 9–12 °C depending on the day and the temperature of the lab). The airflow that is saturated with water vapor at temperature T₁ is subsequently conducted to the mini-climatic chamber at a temperature T₂ (~21 °C; laboratory environment). Consequently, the relative humidity of the mini-climatic chamber is fixed by the following equation

$$\text{RH} = \frac{p_w}{p_{ws}} \times 100$$

where RH is the relative humidity (%), p_w is the partial vapor pressure, and p_{ws} is the saturated vapor pressure at the laboratory temperature (2.64 kPa at 21 °C). Since the flowing air is saturated with water vapor, for example, at 9 °C, the partial vapor pressure is equal to the saturated vapor pressure at T₁(1.26 kPa at 9 °C), and the relative humidity will be settled at ~50%. Our system permits us to control a wide range of relative humidities very precisely; hence, under a phase-contrast microscope and using direct imaging we investigate the kinetics of dissolution of crystals in contact with liquid water and also their deliquescence in contact with water vapor, followed by recrystallization during the evaporation. Experiments were done with unconfined (droplets evaporation) or confined geometries (cylindrical microcapillaries of 500 μm) to investigate the robustness of the results obtained. Measuring the volume change during evaporation of the solution inside the microcapillaries allows

| Table 1. Physicochemical Properties of Salt Solutions Used in This Study |
|------------------|----------------|-----------------|-----------------|----------------|----------------|
| solution | water | NaCl solution 5.95 m | NaCl solution + Fe-mTA (80 ppm) | NaCl solution + Fe-mTA (160 ppm) |
| density (g/cm³) | 1.0193 ± 0.0022 | 1.197 ± 0.0083 | 1.1948 ± 0.0051 | 1.1926 ± 0.0017 |
| surface tension (mN/m) | 71.86 ± 0.05 | 80.53 ± 0.15 | 80.87 ± 0.15 | 80.51 ± 0.2 |
| contact angle on the glass slide (°) | N/A | 20.4 ± 1.8 | 19.6 ± 1.7 | 18.9 ± 2.1 |
| contact angle on the NaCl crystal (°) | N/A | 12.6 ± 1.5 | 12.4 ± 1.5 | 12.5 ± 2.8 |
one to determine the supersaturation at the onset of precipitation; this is done by recording the displacement of the two menisci while simultaneously visualizing the onset of crystal growth in the solution directly with an optical microscope coupled to a CCD camera.

Liquid bridges between mm-scale NaCl crystals are studied as a controlled macroscale caking scenario. First, NaCl crystals are grown for 3 months in Petri dishes by slow evaporation of an initially undersaturated salt solution to obtain large and very pure crystals. Two crystals of similar size and perfectly square corners are glued onto two cover slides, which in turn are attached to a cleaned Corning GlassTM glass slide using double-sided tape in such a way that the crystals touch only at their corners (Figure 3a,b). Salt solution droplets of 1 μL are applied at the contact point, forming a liquid capillary bridge between the two crystals (Figure 3c). An inverted Leica microscope and three-dimensional (3D) laser scanning confocal profilometer (Keyence) are used to investigate the drying of the capillary bridge between the two crystals.

RESULTS AND DISCUSSION

Evaporation-Induced Crystallization. Figure 4 shows the evaporation of droplets of salt NaCl solutions (5.9 molal) with different Fe-mTA concentrations (80 and 160 ppm) on cleaned glass slides at RH = 50% and T = 21 °C. With the evaporation of water, the NaCl concentration increases progressively until the spontaneous precipitation of crystals in the droplets.16,17 For all solutions, i.e., with and without Fe-mTA, the first crystals are formed close to the contact line at the liquid/air interface.16 This nucleation, close to the edge of the droplet, is due to a higher concentration of the solute near the contact line where evaporation is strongest. Clearly, the presence of the additive does not affect the location of the nucleation, i.e., liquid/air interface. For all salt solutions with and without additives, an inward motion of the crystals toward the center of the droplet (Figure 4) can be observed. With the growth of the crystal, it becomes confined between the free surface and the solid substrate; the resulting deformation of the liquid/air interface due to this geometrical constraint results in capillary forces that push the crystal toward the center of the drop.16 For the pure salt solution, as expected, a cubic growth of the crystals is observed after its precipitation (Figure 4, top row). For salt solutions with Fe-mTA, the morphology of the crystal is observed that changes with time: the crystal growth mode starts as cubic at the onset of precipitation, followed by the emergence of significant surface roughness and the development of branched patterns (Figure 4, middle and bottom rows). In addition, in the presence of Fe-mTA, the crystals do not adhere to the substrate like the pure salt after complete drying.

The supersaturation levels ($m/m_s$, with $m_s$ being the concentration at saturation) reached at the onset of crystals precipitation for the salt solutions with and without Fe-mTA

Figure 3. (a) Schematic of the experiment to study macroscale capillary bridges between two salt crystals. (b) Photograph of two NaCl crystals touching at their corners. (c) Liquid capillary bridge formed at the contact point between the two crystals, after depositing a droplet (1 μL) of salt solution.

Figure 4. Temporal evolution of the crystal morphology in drying microdroplets of pure salt (top row), NaCl + 80 ppm Fe-mTA (middle row), and NaCl + 160 ppm Fe-mTA (bottom row).
were determined by evaporation experiments in microcapillaries under the same environmental conditions. The high supersaturation achieved here prior to precipitation in experiments done in such small volumes compared to bulk crystallization is in good agreement with the previously reported results.\(^{13,15,18}\)

In addition, the results, summarized in Table 2, show that there are no major differences between the 80 and 160 ppm as the error bars indeed indicate. However, the difference between the pure salt and salt with m-TA is significant, which shows the role of m-TA as a nucleation enhancer.

In microcapillaries, the crystal growth kinetics after precipitation show exactly the same behavior as for the evaporating droplets: the precipitated crystal grows with a cubic shape at the early stages and after a certain time roughness starts to appear on the faces of the crystal followed by the development of branched patterns at a later stage of growth; the higher the additive concentration, the more branched crystals are formed (Figure 5). The fact that the roughness emerges after a certain time and not at the onset of precipitation at high supersaturation confirms that the interaction of Fe-mTA with the crystalline faces occurs at low saturations. This conclusion has practical implications as it shows that for the additive to be effective, a high level of purity is not needed, i.e., impurities that could induce heterogeneous nucleation at low saturation would even induce a faster interaction of the additives with the crystalline faces.

Because both concentrations of mTA show similar results, in the rest of the discussion of this manuscript, we have chosen to show the case of 160 ppm as a clear example of growth behavior in the presence of mTA. In the microcapillaries, we have studied the growth of cubic crystals before the emergence of any roughness as a function of time for all solutions at the same T, RH, and S. The measurements are done along one side of the crystal in contact with the solution. As seen in Figures 5 and 6, growth is slowed down by the presence of Fe-mTA. This behavior underlines the growth inhibitor role of Fe-mTA. Generally, three growth regimes can be distinguished: first (Regime 1), crystal growth is limited by the integration of the ions into the crystal face and appears linear in time; with the consumption of ions and the decrease of supersaturation (Regime 2), growth becomes diffusion-limited; it is the speed of the ion diffusion in the solution to reach the crystal surface that limits the growth in this regime. As would be expected for a diffusion-controlled growth, a linear relation between the crystal size and the square root of time is obtained (see the inset of Figure 6). However, because the additive impact occurs at low supersaturation, the growth rate (slope of the curve) in this regime is larger for the pure salt than for solutions containing Fe-mTA, confirming again the growth inhibitor role of the additive. Finally (Regime 3), the crystal growth rate decreases slowly and almost stagnates. This could be due to anisotropic growth caused by confinement once the crystal reaches the walls of the capillary.

Deliquescence-Recrystallization Cycles. To study the impact of repeated deliquescence-recrystallization cycles, we allow droplets to dry completely and placed the glass slides with salt crystals inside a mini-climatic chamber at RH = 90% and T = 21 °C under a microscope. NaCl crystals start to take up water because they are in an environment above its equilibrium relative humidity RH_{eq} = 75%, i.e., the deliquescence relative humidity (DRH). The deliquescence of the precipitated crystals from the previously dried droplet is allowed to continue until the last crystal is completely dissolved. The volume of the “new” droplets is found to be approximately the same as that of the initially deposited droplets.

We consider three variables to describe the impact of deliquescence-recrystallization cycling (Figure 7): (1) The time needed to precipitate the first crystal after a droplet is deposited on the glass slide in the first cycle or when the mini-climatic chamber is removed after complete deliquescence in the subsequent cycles; (2) the number of crystals (nuclei) emerging inside the droplet during evaporation; (3) the time needed to observe the morphology transition from cubic to roughened shape in the presence of Fe-mTA.

The first parameter, the crystallization time, shows no measurable dependence on the presence or absence of the anticaking agent. It depends essentially on the solution, substrate, and environment (temperature and relative humidity). It is known that with recrystallization, the number of emerging crystals decreases, as it increases the crystal purity by rejecting impurities.\(^{19}\) This trend is indeed observed in our experiments with pure salt. However, in the presence of Fe-mTA and independent of the amount of additive, more crystals appear with deliquescence-recrystallization cycling. This shows that Fe-mTA acts more as a nucleation promoter with cycling.

The role of the Fe-mTA additive as a nucleation promoter is confirmed by analyzing the time needed to change the morphology of growth. For the first cycle of drying, this time is significantly longer than for the following cycles; the average

### Table 2. Supersaturation (m/m_s) Levels at the Onset of Crystal Precipitation

<table>
<thead>
<tr>
<th>Solution</th>
<th>Supersaturation S at Nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl solution</td>
<td>1.6 ± 0.03</td>
</tr>
<tr>
<td>NaCl solution + 80 ppm Fe-mTA</td>
<td>1.4 ± 0.11</td>
</tr>
<tr>
<td>NaCl solution +160 ppm Fe-mTA</td>
<td>1.5 ± 0.08</td>
</tr>
</tbody>
</table>

Figure 5. Snapshots of evaporation-induced nucleation and growth of sodium chloride crystals in microcapillaries at RH ~ 55% and T = 21 °C. Top: pure NaCl solution (5.95 m); bottom: NaCl solution (5.95 m) + 160 ppm Fe-mTA.
time goes from \( \sim 200 \text{ s} \) in the first cycle to \( \sim 50 \text{ s} \) in the third cycle. This can be explained by the fact that if more crystals precipitate with cycling, the supersaturation will drop quicker, and consequently, the interaction of the Fe-mTA leading to rough crystalline faces will be seen earlier.

Our results show that cycling will lead to multiple nucleations with more roughened crystals; consequently, the effect of Fe-mTA is to make the system evolve toward smaller and rougher crystals with the number of cycles of deliquescence and drying. This outcome is important for harnessing the anticaking effect in practice; smaller crystals are less strongly bonded together since the bridges are smaller, and salt in practice may undergo many deliquescence-drying cycles.

**C-Microscale Effect of Fe-mTA.** To relate our microscale results with evaporating droplets to the macroscale behavior of the anticaking effect of Fe-mTA, we perform macroscale capillary bridge experiments on sets of two macroscopic NaCl crystals in a configuration as explained in Figure 3. Figure 8 shows the drying of the liquid capillary bridges of the pure salt solution and a salt solution with 160 ppm Fe-mTA. With the evaporation of the pure salt solution, a solid crystalline bridge is observed to form between the two grains: this is direct visualization of the caking phenomenon. The two crystals are linked by a continuous and smooth line in which further salt crystallization takes the shape of the concave menisci. In contrast, when the Fe-mTA is added to the salt solution, no crystalline bridge is formed after the water evaporates from the liquid bridge: the two crystals do not stick together. However, a clear roughness starts to form on the crystal surfaces. Quantification of the contact line as extracted from these snapshots (Figure 8c) as well as profilometry of the interface between the crystals (Figure 9) confirm the role of the Fe-mTA in preventing crystallization from solution and in inducing surface roughness instead. Scanning-electron microscopy (SEM) of the crystal interfaces after repeated application and evaporation of liquid capillary bridges (Figure 10) reveals the roughness in the case of Fe-mTA to be of a *snake scale-like* morphology.

Our experiments show that the application of Fe-mTA induces a micron-scale roughness on the crystal surface, which appears as whitening of the crystalline surface. Such roughness has several consequences: at the macro scale: first, it helps to spread the liquid over a larger surface of the crystal and hence reduce the formation of capillary bridges. Second, the formation of such roughness reduces the contact area between the two macrocrystals, which further suppresses the caking phenomenon in the subsequent deliquescence-drying experiments. Moreover, the precipitation of such small crystals makes the surface mechanically weaker than that of the smooth surface of the pure salt crystal, causing them to break more easily. All these factors together, i.e., roughness appearance, smaller contact area, and more brittle surface, explain the anticaking mechanism of Fe-mTA at the macrosopic scale. In addition, such roughness not only avoids the caking phenomenon but also confers antiadhesive properties with respect to other solid substrates such as glass slides or lab plastic Petri dishes in our case.
Figure 8. (a, b) Photographs of the capillary bridges at the contact point of two adjacent crystals after the consecutive deposition of 5 droplets of pure salt solution (a) and of salt solution with 160 ppm Fe-mTA (b). Variation of the contact length after consecutive application of 0–5 droplets of the pure salt solution (two experiments; yellow symbols) and of a salt solution with 160 ppm Fe-mTA (two experiments; green). The lengths were determined from photographs such as shown in (a) and (b), where the red lines indicate the contact lengths. The different curves show the reproducibility of the experiments.
CONCLUSIONS

Understanding the mechanism by which the caking of salt occurs is critical to devising strategies aimed at preventing it. Crystalline solids often cake by the formation of liquid bridges by deliquescence (during periods of high relative humidity) and subsequent recrystallization of microcrystals from solutions (during dry periods). The formation of such solid bridges depends on the material’s particle size and shape and can be influenced by adding anticaking agents. While some anticaking agents act by absorbing excess moisture or by coating particles and making them water-repellent, others interact at the atomic scale with the crystalline grains.

Here, we have investigated the functionality of Fe-mTA, a bio-based anticaking agent originating from the wine industry, which has previously been shown to be quite effective even at very low concentrations (ppm) by weight.

Our results show that, at the microscale, Fe-mTA acts as a nucleation promoter and growth inhibitor by inducing roughness on the surface of crystals; this leads to a snake scale-like morphology at the edges and corners of the crystalline grains at the macroscale. The appearance of roughness, on the one hand,

Figure 9. Microscope image and height profile (along the blue line) for the contact between two salt crystals after application of (a) a droplet of the pure salt solution and (b) salt solution plus 160 ppm Fe-mTA. Red circles indicate surface roughness not encountered in the case of the pure salt solution (bar scale = 500 μm).

Figure 10. SEM images of the contact point between two salt crystals after liquid capillary bridge experiments: (a) droplet of the pure salt solution results in a solid bridge; (b) droplet of a salt solution with 160 ppm Fe-mTA does not result in a solid bridge, instead gives rise to a snake scale-like crystalline surface.
decreases the effective contact area between crystals and, on the other hand, improves the spreading ability of the liquid bridge over the crystalline surfaces. Consequently, the formation of a macroscopic solid crystalline bridge between grains as water evaporates is avoided. In this way, a small amount of Fe-mTA additives not only suppress the caking phenomenon but also gives an antiadhesive quality to the grains with respect to other solid substrates.

We also show that the efficiency of the Fe-mTA anticaking agent does not require a very clean environment; impurities that induce heterogeneous nucleation at low supersaturation will induce an even faster interaction of the additives with the crystalline faces.

These findings open new routes on the use of this additive in other applications such as the food industry, where other types of crystals are used and can have such caking problems. Also, in the field of conservation of cultural heritage, salt crystallization in pores of stones can induce severe damage to artworks due to the development of the crystallization pressure during the growth in the presence of thin films of solution,\(^{1,22}\) the surface roughening and antiadhesive properties elucidated here could be an alternative to avoid the development of the crystallization pressure and consequently reduce damage with salt crystallization in confinement.

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### ABBREVIATIONS USED

Fe-mTA, metal—organic complex of iron (III) and meso-tartrate; L-TA, levo-tartaric acid; D-TA, dextro-tartaric acid; mTA, meso-tartratic acid

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