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Additive Enhanced Creeping of Sodium Chloride Crystals

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ABSTRACT: This article investigates the mechanism behind the creeping of sodium chloride induced by additives. Here, an experimental approach is complemented with theoretical considerations to describe how creeping patterns of brine evolve and how the introduction of additives into the solution affects the morphology of the resultant crystals. We have found that these additives cause kinetic roughening and morphological instability mainly due to the reduction of surface free energy. There was also a marked increase in three-dimensional nucleation of the NaCl crystals and thus branching.

INTRODUCTION

Creeping is a phenomenon observed for many crystalline compounds growing from solution which results in the extension of crystallites across a solid substrate, usually in an unwanted fashion. For example, the creeping tendency is well-known for sodium chloride and can be largely enhanced by the addition of appropriate additives to the solution. We have shown previously that this tendency can be exploited to our advantage, namely, to determine whether an additive is a good anticaking agent for sodium chloride. This is particularly pertinent as caking is one of the main problems encountered during the production, storage, and transport of sodium chloride. When an effective anticaking agent is added to a brine solution, the creeping effect is enhanced and resulting crystallites often show different shapes. Additive enhanced creeping has also been exploited to conserve stonework and statues by reducing damage caused by salt crystallization.

Creeping can be defined as the evaporation-driven extension of crystals on solid, nonporous substrates beginning from the solution rim. In our study, we concentrate on primary (mural) creeping, i.e., the direct growth of the crystals on the surface of the substrate. No attention will be given to secondary (efflorescent) creeping, which is creeping upon previously deposited crystals. The features observed are branched patterns radiating from the central solution source. As classified by Brener et al., there are two different crystal morphologies which can be observed in branched crystal patterns, namely, seaweed and dendritic forms. Seaweed crystal patterns have no pronounced orientational order, whereas those of dendritic patterns have branches in preferred crystallographic directions. These can be further classified into fractal and compact patterns, which depend on the value of the Hausdorff dimension, but this will not be covered in our paper. We have previously found that the creeping patterns we observe in the case of NaCl with additives show seaweed type growth (the crystals have no precise orientational order).

The aim of this paper is to describe the mechanism of how the chosen additives act on the sodium chloride crystals and the impact on their creeping patterns that come about. This will be done using an experimental approach, imaging how the crystallites grow from solution droplets in the presence of different additives. The influence of the additives is explained using a theoretical model.

Theoretical Considerations. In our semiquantitative model, we consider additives that adhere quite well to the growing crystal surface. This adhesion leads to two important effects: first, a lowering of the surface energy which allows easier nucleation, and second, a blocking at the surface which leads to slower growth of specific crystals and increased supersaturation. This increase in supersaturation leads again to an increase in the three-dimensional (3D) nucleation and kinetic roughening due to the decrease in surface binding energy. If homogeneous or secondary 3D nuclei are easily formed, enhanced branching of the growth features is expected and seaweed patterns are likely to develop. The difference in creeping growth of NaCl in the absence and presence of additive is schematized in Figure 1.

Surface Free Energy. To get a better understanding of the effect of supersaturation and additive content on the creeping process, we first estimate the influence of additive on surface free energy. The additive surface coverage, θ, is defined as the fraction of the crystal surface area covered by additive (0 ≤ θ ≤ 1):

Received: January 6, 2017
Revised: March 24, 2017
Published: April 26, 2017
\[ \theta = n_a \frac{F}{A} \]  

with \( n_a \) the number of additive molecules per surface site of area \( A \), and \( F \) the surface area covered by one adsorbed additive molecule. Estimation of \( \theta \) is done by using the simple Langmuir adsorption model.\(^{11} \) This model states that the fraction of surface area covered by additives, \( \theta \), is given by

\[ \theta = \frac{Kc}{1 + Kc} \]  

with \( c \) the additive concentration in solution and \( K = k_{\text{ad}}/k_{\text{des}} \) the ratio of adsorption probability and desorption probability of additive for a given surface area \( F \). So, the fraction of free surface area is

\[ \theta^* = (1 - \theta) = (1 + Kc)^{-1} \]  

As was pointed out by Gibbs a (partial) surface coverage of additives leads to a lowering of the surface free energy, according to his adsorption isotherm.\(^{12} \)

\[ d\sigma = -\Gamma d\mu_a \]  

with \( \sigma \) the surface free energy, \( \Gamma \) surface concentration (number of additive molecules per surface area), and \( \mu_a \) the thermodynamic potential of the additive in the solution,

\[ \mu_a = \mu_a^0 + kT \ln c \]  

Here \( T \) is temperature and \( k \) is Boltzmann’s constant. It is necessary that the adsorbed additives prohibit further addition of growth units at the surface.\(^{13} \)

From eq 4 and

\[ d\mu_a = kT d\ln(c) = kT \frac{dc}{c} \]  

we obtain

\[ \frac{d\sigma}{dc} = -\frac{kT \Gamma}{c} \]  

Using \( \Gamma = \frac{\theta}{F} \) with \( F \) the surface area occupied by one adsorbed additive molecule we get

\[ d\sigma = -\frac{kT}{c} \frac{Kc}{1 + Kc} \frac{1}{F} dc \]  

Integration of eq 8 gives the decrease in surface free energy:

\[ \Delta\sigma = -\frac{kT}{F} \ln(1 + Kc) = \frac{kT}{F} \ln(1 - \theta) \]

So, the surface free energy as a function of additive adsorption is

\[ \sigma = \sigma_0 + \frac{kT}{F} \ln(1 - \theta) \]

with \( \sigma_0 \) the surface free energy of a “clean” surface, i.e., in contact with pure brine. Figure 2 displays the decrease of surface free energy of (100) NaCl in contact with saturated brine as a function of \( \theta \), starting from a clean (100) NaCl surface in brine, with \( \sigma_0 = 38.10^{-3} \) J/m\(^2\)\(^{14} \) and \( F = 0.6 \times 10^{-18} \)

![Figure 1. Difference in crystal growth of NaCl in the (a) absence and (b) presence of additive.](image)

![Figure 2. Surface free energy of (100) NaCl in contact with saturated brine as a function of additive surface coverage, \( \theta \).](image)
m^2 (Table 1). This reduction in surface free energy with increasing additive coverage promotes morphological instability during crystal growth.

| Parameter                     | Value        |
|-------------------------------|--------------|
| volume growth unit, \( \Omega \) | \( 22.43 \times 10^{-30} \) m^2 per ion |
| temperature, \( T \)          | 300 K        |
| Boltzmann’s constant, \( k \) | \( 1.38 \times 10^{-23} \) J/K         |
| surface area of one additive unit, \( F \) | \( 0.6 \times 10^{-18} \) m^2 (for Fe(CN)_6) |
| surface free energy clean (100) NaCl, \( \sigma_0 \) | \( 38 \times 10^{-3} \) J/m^2 |
| kinetic constant: \( C/A \)   | \( C/A \) is arbitrarily set to 1 |

**Kinetic Roughening, Growth Rate, and Supersaturation.** As pointed out by Sears,\(^{13}\) the above not only holds for the crystal surface, but also for the free energy of the growth steps. The step free energy lowers by adsorption of additive, and in combination with the high supersaturation during creeping this leads to kinetic roughening\(^{15}\) as can be concluded from the nonfaceted crystallites during our experiments.

The kinetically roughened crystal faces grow according to the Wilson–Frenkel mechanism,\(^{16}\) following

\[
R = A(1 - \theta)[\exp(\Delta \mu/kT - \Delta \mu_0/kT) - 1]
\]

in which the growth rate is retarded because part of the surface is covered by additive, \( \theta \). We here assume a dead supersaturation zone,\(^ {17}\) \( \Delta \mu_0/kT \), where growth is governed by two-dimensional (2D) nucleation and blocking by incorporation of the additives.\(^ {18}\) Therefore, we approximate \( R(\Delta \mu < \Delta \mu_0) = 0 \). Further, \( A \) is only weakly dependent on surface free energy\(^ {19}\) and \( \Delta \mu_0/kT \) tends to increase with additive coverage.\(^ {17,18}\)

The rate limiting step in creeping is determined by solvent evaporation.\(^1\) Here crystal growth follows the rate of solvent evaporation and is in first approximation independent of additive concentration. This implies that the driving force for crystal growth has to adapt to a given growth rate \( R_0 \) determined by solvent evaporation. \( R_0 \) from eq 11 this gives

\[
\frac{\Delta \mu}{kT} = \ln \left( \frac{R_0}{A(1 - \theta)} + 1 \right) + \frac{\Delta \mu_0/kT}{\Delta \mu/kT}
\]

So, for creeping an increased additive coverage results in a larger driving force for crystal growth. The combination of a higher driving force and a lower surface/step energy promotes the occurrence of kinetic roughening and thus morphological instability. Of course, a larger \( R_0 \) induced by lowering the solvent partial pressure during the creeping process also increases \( \Delta \mu_0/kT \).

**Competition between 3D Nucleation and Crystal Growth.** The formation rate of spherical 3D nuclei at/near the tips of the creeping branches is given by\(^ {20}\)

\[
J = C(1 - \theta) \sigma^{3/2} \exp(\Delta \mu/kT - \Delta \mu_0/kT) \exp \left[ - \frac{B\sigma^3}{\Delta \mu^2} \right]
\]

In this equation \( C \) is a kinetic constant and \( \sigma \) is given by eq 10. Further,

\[
B = f \frac{16\pi \Omega^2}{3kT}
\]

with \( \Omega \) is the volume of one growth unit and \( f \leq 1 \), being a correction term for heterogeneous 3D nucleation. As the second exponential term in eq 13 is determined by thermodynamics, rather than kinetics, here no correction for \( \Delta \mu_0/kT \) is applied. It is clear from eq 13 that the rate of 3D nucleation rapidly increases for increasing supersaturation and decreasing surface free energy. To understand the effect of 3D nucleation on the creeping patterns, it is helpful to compare the 3D nucleation rate with the crystal growth rate. This gives an indication of the relative amount of microcrystallites and branching in the growth patterns.

In our model, we only consider homogeneous nucleation, i.e., \( f = 1 \), as in our seaweed creeping patterns the crystallite grains are not epitaxially related. In view of the high supersaturation involved during creeping growth, we also neglect the dead supersaturation zone, i.e., \( \Delta \mu_0/kT \cong 0 \).

It then follows from eqs 10, 11, and 13 that the ratio of 3D nucleation rate and crystallite growth, \( R \) is

\[
R = \frac{J}{R} = \frac{C}{A} \frac{\exp(\Delta \mu/kT)}{\exp(\Delta \mu/kT) - 1} \left[ \sigma_0 + \frac{kT}{F} \right] \ln(1 - \theta)^{3/2} \left[ -B \left( \sigma_0 + \frac{kT}{F} \ln(1 - \theta) \right)^2 \right]
\]

and is displayed in Figure 3 as a function of \( \Delta \mu/kT \) for different \( \theta \) values and in Figure 4 as a function of \( \theta \) for different \( \Delta \mu \). As input the data given in Table 1 is used.

![Figure 3. Ratio 3D nucleation rate and growth rate, R, as a function of supersaturation, \( \Delta \mu/kT \), for six different surface coverages, \( \theta \).](Image)

From the two graphs, it is clear that the 3D nucleation rate with respect to growth rate increases rapidly with supersaturation and additive coverage, the latter due to an increased additive concentration in the solution. This leads to an enhanced microcrystallite formation and branching of the creeping patterns. The introduction of \( f < 1 \) or a finite value of \( \Delta \mu_0/kT \), a higher \( \sigma_0 \) (63 mJ/m^2)\(^{21}\) or lower \( \sigma_0 \) (24.4 mJ/m^2)\(^{22}\) changes the situation somewhat, but does not alter the general conclusions. It follows from eq 11 that if \( \Delta \mu < \Delta \mu_0 \) no growth occurs and nuclei cannot expand. Therefore, eq 15 only holds if
The third additive chosen is a branched amide compound, nitrilotriacetamide (NTAA) as per Nobel. Nitrilotriacetamide has been previously reported in the literature to have an effect on the growth of NaCl at a specific pH, of approximately 4.2.24

Creeping Tests. The creeping tests performed in this investigation were all performed on glass microscope slides, previously washed with ethanol and dried with a dust free tissue, to minimize external effects. Saturated brine solution (solubility NaCl 359 g L\(^{-1}\) water at 25 °C) was combined with the chosen additive, to give a solution containing concentrations of the additive in a range from 0.001 to 1% (w/w) with respect to the solution. A filtered 5 \(\mu\)L droplet of solution was placed on the microscope slide and placed into a climate chamber set at a fixed temperature of 20 °C and relative humidity of 50%. The droplet was allowed to evaporate, and the resulting creeping patterns were imaged using a Leica Wild M10 stereomicroscope and a FEI scanning electron microscope. These experiments were performed using all concentrations of additive as shown in Table 2. As the contact angle of the solution with the substrate can be important in the case of creeping, this was also measured for each solution using an optical setup imaging the droplets viewed from the side by a CCD (values stated in Table 2). As there was little variation between the contact angles of each solution on the substrate, the effect was not considered during interpretation of the results. Also the experiments containing 0.001% (w/w) additive showed very little difference to the control; therefore these are not discussed in this paper. In addition, the pH of the individual solutions was measured, and all experiments were performed in triplicate to ensure reproducibility.

In Situ Optical Microscopy. In order to visualize the evaporation of the droplets at higher magnification in situ, samples were prepared as above, but instead of being stored in a climate chamber, they were placed under a Leica DMRX optical microscope and allowed to evaporate at ambient temperature (on average 20 °C, ~50% relative humidity). The propagation of the droplet evaporation was imaged at a rate of 1 frame per second in transmission mode, and a resulting movie was made using an amalgamation of the images. Singular images are displayed in the results section, and movies of Figures 7 and 9 are included in the Supporting Information, Film 1 and Film 2. These experiments were performed with concentrations of 1% and 0.1% (w/w) additive in the brine solutions.

Scanning Electron Microscopy. In order to observe the crystal patterns at a higher magnification and a higher depth of field than feasible with optical microscopy, we used scanning electron microscopy (SEM). The creeping patterns were fully dried in a climate chamber at 20 °C and 50% R.H. and then sputtered with Au using a Cressington 108 auto sputter coater. The samples were imaged using a FEI Phenom scanning electron microscope in backscattering mode at 5 kV.

EXPERIMENTAL RESULTS AND DISCUSSION

From the theory section, we can summarize the following points on the effect that impurities have on the crystallization of a material during creeping: (1) they lower the surface free energy, (2) they cause kinetic roughening, also because of the higher supersaturations involved, (3) they enhance heterogeneous/homogeneous 3D nucleation, (4) they promote branching.

These conclusions will be verified by experiments in this section. Qualitative results can be obtained from this investigation; however, it is impossible to produce quantitative information as the surface coverage cannot be measured in situ for creeping and the supersaturation at the crystal–liquid interface is also difficult to determine in these situations.

As a reference sample, a saturated solution of NaCl was dropped onto a microscope slide using the above indicated method and allowed to dry at 20 °C and 50% R.H. This pattern was observed using optical microscopy and SEM, as shown in Figure 5. It is evident that there is little to no roughness on the surface of the perfectly faceted cubic crystals. Here crystal growth proceeds by a layer by layer mechanism (no kinetic roughening), and the number of 3D nuclei formed is limited. There is also very little evidence of creeping.

To estimate the supersaturation at which the crystals first begin to nucleate from a saturated brine droplet with no additive, an evaporating droplet on a glass substrate was weighted in situ using a precision balance. From the change in weight of the droplet when the first crystallites appeared as imaged using optical microscopy, we arrived at an approximate average figure of \(\Delta \mu /kT \approx 0.06\). As the
facets of the crystals are significantly destabilized by Fe(CN)$_6$.
Destabilization of the cubic morphology is also evidenced by the occurrence of hopper-like growth, which is a manifestation of morphological instability as well (Figure 8b). Both nonfaceted morphologies point to kinetic roughening due to low surface energy and high supersaturations, which matches with our theoretical inferences.

Figure 9 shows the evolution of the creeping pattern of a saturated NaCl solution containing 0.1% (w/w) Fe(CN)$_6$. It was observed that the NaCl crystallites again span outward from the droplet boundary in a branched seaweed fashion, with no definite orientational order. Again, it is evident that the individual crystallites are weakly attached to one another and so arrange in a seaweed branched pattern. The individual crystallites exhibit a dendritic pattern, with spikes pointing toward the <100> directions (Figure 9b).

With a decreasing amount of additive, there is less outward spread of the branches but with the same strong morphological instability as evident in the 1% (w/w) Fe(CN)$_6$ case. To obtain an idea of the supersaturation for the NaCl growth with 1% Fe(CN)$_6$ additive, a similar droplet evaporation experiment as for the pure NaCl solution was carried out. This gave an average supersaturation of $\Delta \mu/\mu T \approx 0.20$, which is beyond the value of $\Delta \mu/\mu T \approx 0.06$ for pure brine. This points to a large dead supersaturation zone, as was previously reported for the same NaCl-additive system in ref 28. When growth sets on, branching immediately takes place as predicted by eq 15, regardless of $\Delta \mu/\mu T$. The dramatic change in nucleation rate and morphology indicates that the surface coverage of Fe(CN)$_6$ must be high. A high occupancy (~52%) of Fe(CN)$_6$ of [100] NaCl was also observed by surface X-ray diffraction, although at different conditions.79

Iron Meso-tartrate (Fe-mTA) as Additive. In a similar fashion to that observed for the creeping pattern of NaCl with Fe(CN)$_6$, there is a marked difference in the NaCl creeping patterns with decreasing amounts of Fe-mTA additive, as displayed in Figure 10. The spread of the branched patterns observed for that with 1% (w/w) Fe-mTA is not as wide as observed for Fe(CN)$_6$, but the cubic growth is very disrupted. For the lowest additive concentration of 0.01% (w/w), there is a tendency toward cubic growth.

For 1% and 0.1% (w/w) concentrations, the evolution of the creeping pattern begins at the peripheries of the droplet with branched patterns composed of singular crystals, which are morphologically unstable, and showing no evidence of cubic shape. This morphological instability is particularly evident in Figure 11a. More crystals nucleate until the entirety of the droplet edge is filled with crystallites. The solution then begins to flow outward over the deposited crystals (Figure 11b). It is evident that the crystallites in the outward flowing solution are not attached to each other when they are formed, and the solution flows over and around them until the liquid layer is low enough that the crystallites deposit onto the substrate in a chain to form the macroscopic seaweed branches of the creeping pattern. The individual microscopic crystallites are morphologically unstable with no clear shape to them.

At a higher magnification of these branches, the SEM images show that there is a large amount of said morphological instability on the surface (Figure 12). It also indicates repeated 3D heterogeneous nucleation of numerous microcrystallites. No <100> spikes were observed growing in the <100> directions, as in the case of FCN.
Figure 12b shows that morphological instability is still present at lower additive concentrations of 0.1% (w/w) Fe-mTA, with an extremely rough surface with no visible fully faceted crystallites. Instead, the surface is dominated by a chaotic growth pattern due to the lower surface energy and fast growth times. For both additive concentrations, there is also evidence of hopper growth, which is an indication of morphological instability as well.

Our experimental findings in this case also link well with our theoretical work, as we have shown that Fe-mTA enhances the roughening of the crystal surfaces and the branching of the crystal creeping pattern, which is a result of the lowered surface energy and surface blocking. It is also evident from our results that there is a large increase in 3D nucleation, in comparison to that of the control.

Nitrilotriacetamide (NTAA) as Additive. In a similar fashion to the two previous examples, the decrease in additive concentration leads to a decrease in crystallite growth (Figure 13). However, in the case of NTAA, the lowest concentration of 0.01% (w/w) still has a markedly noncubic growth pattern. In all cases when using NTAA as the additive, there is little dendritic spread, resulting in a far more compact pattern than previously observed with Fe(CN)₆ and Fe-mTA. Therefore, this does not fully agree with our model outlined in this article.
In the case of the evaporation of a brine solution containing 1% (w/ w) nitrilotriacetamide, the creeping pattern is markedly different from that observed when using 1% Fe(CN)₆ and Fe-mTA. This can be seen in Figures 14 and 15. The growth of the crystallites begins at the periphery of the droplet, but the outward spread of the initial crystallites is much more limited than that of the other two cases, leading to a more compact pattern. The salt crystals in this case are not in the expected cubic form, but instead display a needle-shaped morphology. Powder X-ray diffraction measurements have been performed to confirm that these needles are indeed made from NaCl and not the additive.

Figure 11. (a, b) Optical microscope images of the evolution of the creeping pattern of a saturated NaCl solution containing 1% (w/w) Fe-mTA.

Figure 12. Scanning electron microscope images of the creeping pattern of a saturated NaCl solution containing (a) 1% (w/w) Fe-mTA and (b) 0.1% (w/w) Fe-mTA.

Figure 13. Creeping patterns of a saturated brine solution containing (a) 1% (w/w) NTAA, (b) 0.1% (w/w) NTAA, (c) 0.01% (w/w) NTAA.

Figure 14. Optical microscope in situ images of the creeping pattern of a saturated NaCl solution containing 1% (w/w) NTAA. The time interval between successive patterns is approximately 30 s.

The needles spread outward over the glass substrate but also inward into the center of the droplet, leading to a complete coverage of the center of the creeping pattern with layers of criss-cross NaCl needles. No branching of the needles is observed, which disagrees with the theory.

Scanning electron microscopy shows that the entire surface of the creeping pattern consists of thin criss-cross needles of NaCl, of approximately 1–5 μm in width (Figure 16a). The theory outlined in this paper does not explain the formation of this type of growth. The reason for the evolution of these needle crystals, which violate the m̅3m point group symmetry of NaCl, will be further outlined in a forthcoming publication. However, our results here do agree with the
We have found that when using nitrilotriacetamide as an additive, we do not observe the expected branching pattern, but instead a dense pattern consisting of ultrathin NaCl needles. Therefore, the model does not fully explain the mechanism of this creeping pattern, which is a topic of further investigation.

**CONCLUSIONS**

During this investigation, we have observed multiple changes in the morphology of sodium chloride creeping patterns which can be attributed to the introduction of various additives into a brine growth solution. We have also shown that the rate of 3D nucleation increases rapidly with increasing supersaturation and additive concentration. This leads to a branched crystal pattern consisting of numerous nonfaceted microcrystals, which was observed for the cases of ferrocyanide and iron meso-tartrate as additives. These observations have been explained using a semiquantitative model, which postulated that the additive coverage on the surface of the sodium chloride crystals leads to a decrease in the surface free energy and therefore an increase in morphological instability and kinetic roughening.

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**ACKNOWLEDGMENTS**

We would like to acknowledge Akzo Nobel Industrial Chemicals for the funding of this project.
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