

## **The effect of ferrocyanide ions on sodium chloride crystallization in salt mixtures as studied by NMR**

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### **Abstract**

The use of crystallization inhibitors such as ferrocyanide has been proposed as a potential preventive treatment against salt damage of historical monuments. It has been extensively tested for crystallization of single salts, where it has shown to be effective. However, in practice there are always mixtures of salts present. Therefore, before using inhibitors in practice, there is a strong need to explore their effect on salt mixtures. A main obstacle is the measurement of the individual salt concentration in a mix, which is necessary to determine the ternary phase diagram. We have developed a NMR setup in which we are able to measure quasi-simultaneously Na, Li and H, giving the possibility to measure both the Na and Li concentration. We have also incorporated a digital microscope, giving the possibility to perform time-lapse microscopy of the crystallization. This gives the possibility to connect the measured concentrations in a mixture with the visual point of crystallization. In this research, we studied the effect of ferrocyanide ions on NaCl crystallization as single salt and in a mixture with LiCl. A series of micro droplet drying experiments was undertaken. For a NaCl solution droplet, in the presence of the inhibitor, a significantly higher supersaturation, in the order of 10 M, prior to the onset of crystallization and a change in crystal morphology were observed. For the mixtures of NaCl - LiCl, the NaCl supersaturation was much lower in the presence of the inhibitor than for the single salt. However, a significant change in the crystal morphology was seen in the presence of inhibitor for these salt mixtures.

**Keywords:** salt mixture, crystallization, drying, inhibitor, NMR

## 1 Introduction

The use of crystallization inhibitors has been proposed as a potential preventive treatment against damage and is extensively tested for crystallization of single salts. However, in practice salt mixtures are present. To stop or reduce salt damage, preventive methods are required. In the past, intensive research has been carried out to test various protective treatments; however, all these tests have been performed on single salts, which are rarely found in practice, where always salt mixtures are present. The crystallization behavior of mixed salt systems is much more complicated than that of pure single salts. For instance, the crystallization of one salt from a mixture does not occur at a specific value of the relative humidity, but rather across a range of values [1]. The crystallization of salt mixtures occurs at lower humidities than expected for single salts [1]. Few studies have been carried out to understand the crystallization behavior of salt mixtures [1-3]. Linnow et al. have reported a study in which the complexity of the kinetic and thermodynamic properties of the salt mixtures is considered [1]. The authors investigated the crystallization sequence of complex salt mixtures using Raman microscopy and polarization microscopy. This work has been extended by De Clercq et al., who studied the crystallization behavior of this mixture in porous limestones [2].

Recently, the use of crystallization inhibitors has been proposed as a potential preventive treatment. These inhibitors are known to act either by preventing or by delaying the onset of nucleation and hence crystallization or by changing the crystal growth mechanism by adsorbing onto specific crystal faces. Ferrocyanide,  $[\text{Fe}(\text{CN})_6]^{4-}$ , is one of the most researched crystallization inhibitors against NaCl damage. For bulk solutions, an increase in NaCl supersaturation has been reported in the presence of ferrocyanide ions [4, 5]. If such a supersaturation can be sustained inside a porous material it can be dangerous for the material. However, recently it has been shown that no high supersaturation is generated inside building materials in the presence of ferrocyanide ions [4, 6]. Additionally, ferrocyanide ions promote the formation of non-destructive efflorescence on building materials [6]. However, to the best of our knowledge, no studies have been reported where the influence of ferrocyanide ions on salt mixture has been studied. The reason is the difficulty to measure simultaneously different types of ions during in-situ measurements. However, with the help of a specially designed NMR set-up, we are able to

measure H, Na and Li ions simultaneously during dynamic drying experiments. The concentration of dissolved salt ions can be calculated from the ratio of the Na / H content and the Li / H content. In this work, we focused on the effect of ferrocyanide ions on the drying and crystallization behavior of NaCl in mixtures with LiCl. All drying tests have been performed in salt solution droplets.

## 2 Experimental setup

In this study, a specially designed Nuclear Magnetic Resonance (NMR) set-up was used. NMR is used for carrying out non-destructive, quantitative and simultaneous measurements of hydrogen (H), sodium (Na) and lithium (Li) ions in the droplet. NMR is based on the principle that in a magnetic field, nuclei have a specific resonance frequency and can be excited by a radio frequency field. The resonance frequency  $f$  (Hz) depends linearly on the magnitude of the magnetic field:

$$f = \gamma/2\pi B_0 \quad (1)$$

where,  $\gamma/2\pi$  (Hz T<sup>-1</sup>) is the gyromagnetic ratio and  $B_0$  (T) is the main magnetic field. The signal intensity ( $S$ ) of a spin echo as used in the experiment is given by:

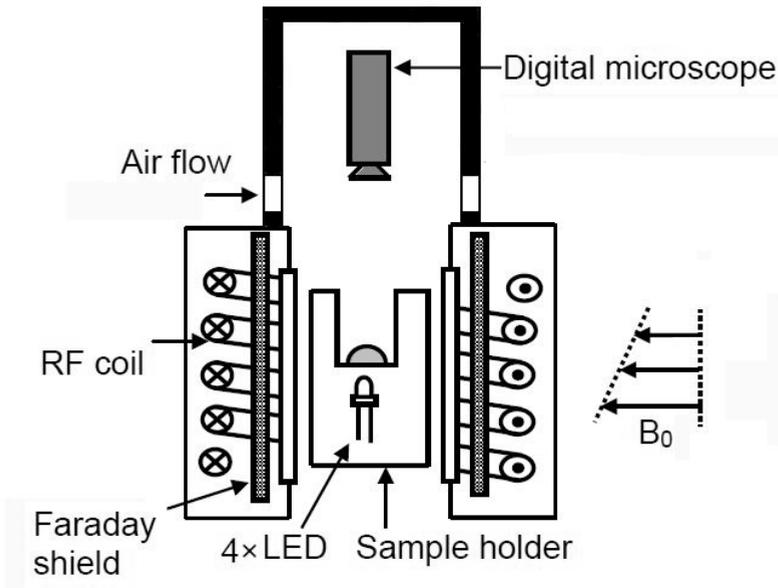
$$S = k \rho \exp(T_e/T_2)(1 - \exp(-T_r/T_1)) \quad (2)$$

where  $S$  is the signal intensity,  $k$  is the sensitivity of the nuclei relative to hydrogen,  $\rho$  is the density of the nuclei,  $T_r$  and  $T_1$  are the repetition time of the pulse sequence and spin-lattice relaxation time,  $T_e$  and  $T_2$  are the spin-echo time and spin-spin relaxation time. The gyromagnetic ratio ( $\gamma/2\pi$ ), the magnitude of the nuclear spin ( $I$ ), the relative NMR sensitivity, and the values of  $T_1$  (spin-lattice relaxation time) and  $T_2$  (spin-spin relaxation time) of the H, Na and Li nuclei are given in table 1.

**Table 1:** The gyromagnetic ratio, magnitude of the nuclear spin, relative NMR sensitivity, and  $T_1$  and  $T_2$  values for H, Na and Li nuclei.

Nucleus	$^1\text{H}$	$^{23}\text{Na}$	$^7\text{Li}$
Spin ( $I$ )	1/2	3/2	3/2
$\gamma/2\pi$ (MHz/T)	42.58	11.26	16.55
Relative sensitivity	1	0.093	0.29
$T_1$ (ms)	2670	75	2502
$T_2$ (ms)	2000	30	1793

Using NMR we can selectively measure just H, Li or Na. For the experiments presented in this chapter, a home-built NMR scanner with a static magnetic field of 0.78 T was used, which can quasi simultaneously measure both H, Na and H. A schematic diagram of the setup is given in Figure 1.

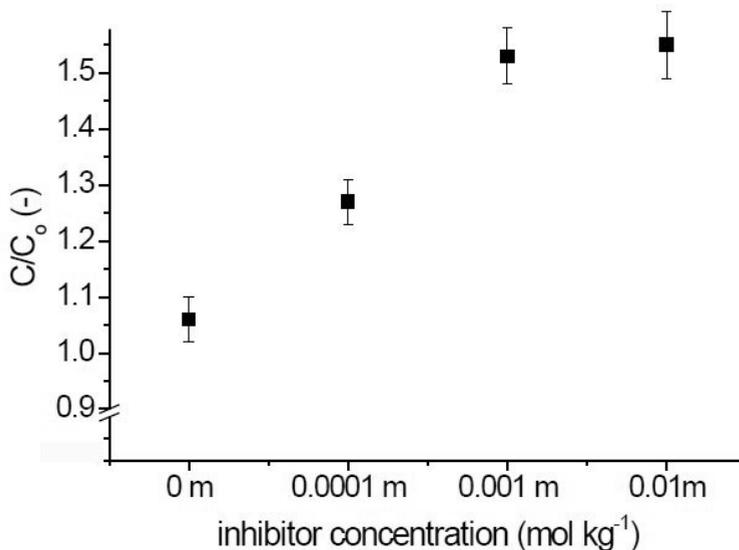
**Figure 1:** A schematic diagram of the NMR set-up for the droplet drying experiments. A 300  $\mu\text{L}$  droplet of NaCl and NaCl-LiCl mixture was placed on the glass holder after which the drying was started.

An extensive description of this set-up can be found elsewhere [6, 7]. The signal is obtained only from the dissolved Na, Li and H nuclei, because the signal from the nuclei incorporated in the crystals decays too fast to be detected. To obtain a sufficient signal-to-noise ratio, 256 and 64 averages of the spin echo measurements are taken for sodium and lithium ions, respectively. The magnetic field gradient was chosen such that the whole droplet is covered in a measurement. To obtain visual information time-lapse microscopy of the crystallization was performed using a Dino-lite® digital microscope along with the NMR measurements. Using NMR, the average concentration ( $C_{avg}$ ) is determined over the whole volume of the droplet. The drying was carried out at room temperature. A 300  $\mu$ L salt solution droplet was placed on a cylindrical quartz sample holder and airflow of about 1 L min<sup>-1</sup> was used to control the humidity in the Perspex chamber.

### 3 Results and discussion

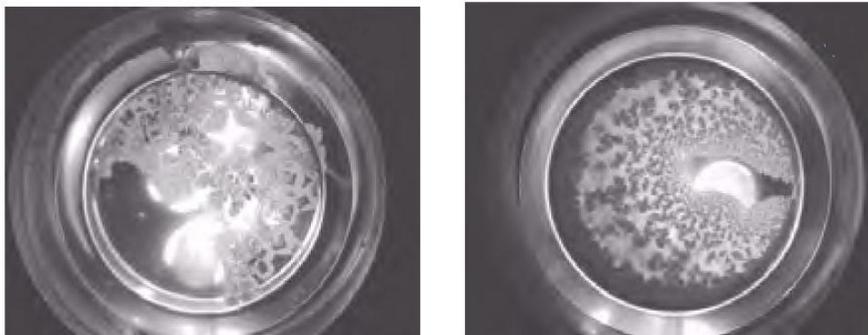
#### 3.1 Single salt solution of NaCl

In this study potassium hexa-cyanoferrate (II) tri-hydrate  $K_4[Fe(CN)_6] \cdot 3H_2O$  was tested as a crystallization inhibitor. First, the influence of ferrocyanide inhibitor on NaCl crystallization was studied. For this purpose, droplets of NaCl solution with and without inhibitor were dried inside the NMR set-up. Using NMR, the hydrogen and dissolved sodium content was measured and using the digital microscope, the onset of crystallization and crystal morphology were recorded. From the ratio of the Na and H content (Na / H), the NaCl concentration is calculated. We have studied the effect of various inhibitor concentrations on NaCl nucleation (supersaturation), crystal size and crystal morphology. For this purpose 0.0001 m, 0.001 m and 0.01 m inhibitor concentrations were tested. For the single salt, NaCl supersaturation can be calculated as  $C_{NaCl} / C_{NaCl,o}$ , where  $C_{NaCl}$  is the measured NaCl concentration and  $C_{NaCl,o}$  is the saturation concentration of NaCl (6.14 m).



**Figure 2:** The supersaturation as measured using NMR plotted as a function of the concentration of the inhibitor used.

The results are shown in Figure 2, where supersaturation is plotted as a function of inhibitor concentration. For the droplet without inhibitor, the onset of crystallization was observed at a concentration of  $6.3 \pm 0.5$  m, giving a supersaturation of  $1.03 \pm 0.08$ . In the presence of inhibitor, the crystallization was observed at a concentration higher than the saturation concentration of NaCl; that is, the droplet supersaturates. The supersaturation increases with increasing inhibitor concentration. A maximum supersaturation of 1.55 is observed for 0.01 m inhibitor. These results clearly indicate that ferrocyanide ions act as a strong nucleation inhibitor for NaCl crystallization. The results are in line with other studies, where higher supersaturation in the presence of ferrocyanide ions was reported. The inhibiting action of ferrocyanide ions on NaCl crystallization can be caused by the fact that they can reduce the concentration of the available solvent, i.e., water, in the system, thereby increasing the relative supersaturation, and by adsorbing  $\text{Na}^+$  ions they can interfere with ion transport towards more or less developed NaCl clusters with dimensions below the critical radius.



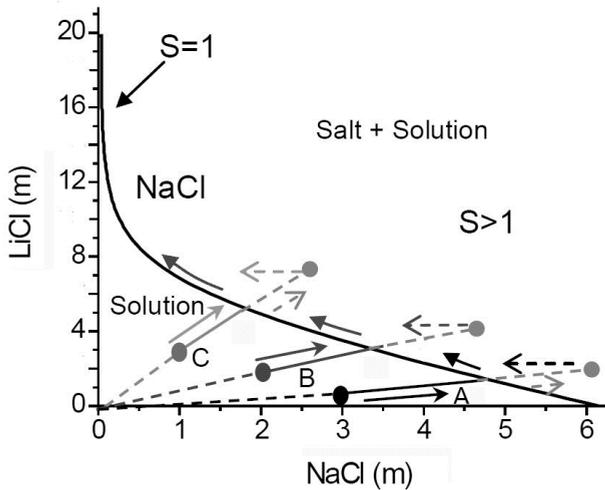
**Figure 3:** Images showing the crystal morphology at the end of a drying experiment: (left) with no inhibitor (right) with 0.01 M inhibitor

The digital microscope images in Figure 3 show that ferrocyanide also acts as a habit modifier for NaCl. In case of drying of a NaCl solution droplet without inhibitor, cubic crystals were seen growing at the liquid/air interface, whereas, in the presence of inhibitor dendritic crystals first form at the liquid/air interface. These crystals then spread very rapidly all over the substrate. Spreading of the crystals was more extensive at higher inhibitor concentration. The branches of dendritic crystals provide a pathway for spreading of solution over a much larger surface area. This phenomenon is commonly known as 'salt creep'.

### 3.2 Salt mix of NaCl-LiCl-H<sub>2</sub>O

In the case of salt mixtures having one ion in common (e.g. NaCl - KCl and NaCl - LiCl), due to an additional chlorine (Cl) from the second salt, supersaturation  $S \neq C_{NaCl} / C_{NaCl,o}$ . For a mixture of monovalent salts, e.g., NaCl - KCl, supersaturation is defined as,  $S = [a / a_o]^{1/2}$ , where,  $a = C_{NaCl} (C_{NaCl} + C_{KCl})$  and  $a_o = C_{NaCl,o} (C_{NaCl,o} + C_{KCl,o})$ , where  $C_{NaCl}$  is the actual concentration of sodium chloride and  $C_{KCl}$  is that of potassium chloride. The index 'o' refers to the saturation concentration. The concentration (C) in this work is defined as the number of moles of salt dissolved in one kilogram of solvent (molality). In this study we have looked at a mixture of NaCl and LiCl, as we can measure simultaneously the H, Na and Li ions. From the concentrations of both the Na and Li ions, we can determine the exact location of the mixture in the phase diagram. This way, it was possible to check whether the equilibrium solubility line is followed after

the onset of crystallization. The ternary phase diagram of a NaCl-LiCl-H<sub>2</sub>O mixture at 25 °C is given in Figure 4, where LiCl concentration is plotted as a function of NaCl concentration. The solubilities were calculated using the Pitzer electrolyte solution model [8]. The ion interaction model parameters for LiCl (aq) and NaCl - LiCl mixed solutions were obtained from experimental water activity data (LiCl) and solubilities in the ternary system at 25 °C [9]. The calculated solubilities in Figure 4, agree with available experimental data within the expected experimental uncertainty of  $\pm 0.05 \text{ mol kg}^{-1}$ . The solubility equilibrium line is shown by a solid black line. Everywhere on this line NaCl will crystallize and LiCl will precipitate only at very high concentrations (viz., 19.84 m LiCl and 0.03 m NaCl). As an example, the expected paths during evaporation of a solution are shown by the solid lines A, B and C for three different initial ion concentrations.

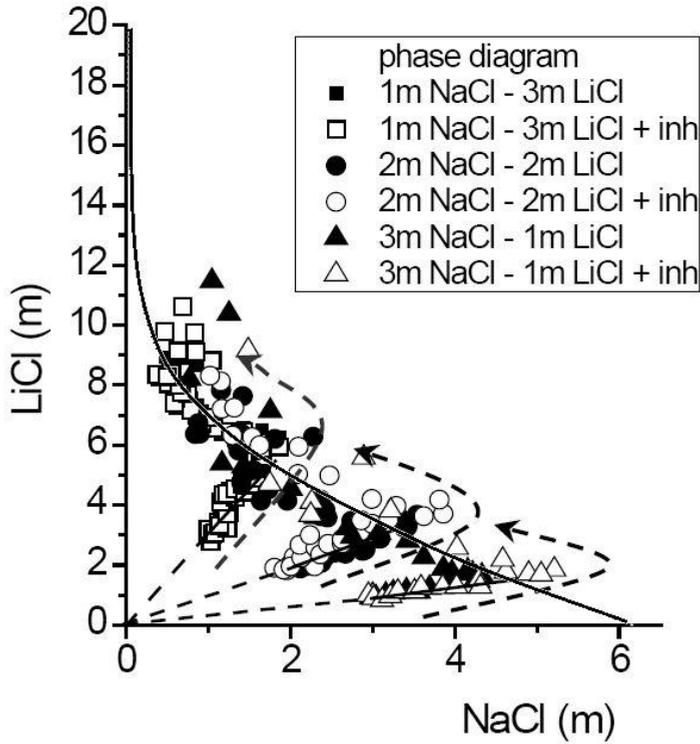


**Figure 4:** The ternary phase diagram of NaCl-LiCl-H<sub>2</sub>O at 25°C. During evaporation the paths A, B and C will be followed for salt mixture of compositions 1 m NaCl - 3 m LiCl, 2 m NaCl - 2 m LiCl, and 3 m NaCl - 1 m LiCl, respectively. If no crystal appears at the intersection of path A, B, C and the equilibrium line ( $S = 1$ ), the concentration will keep on increasing (supersaturation), as indicated by dashed lines. After crystallization the system will return to the equilibrium solubility line.

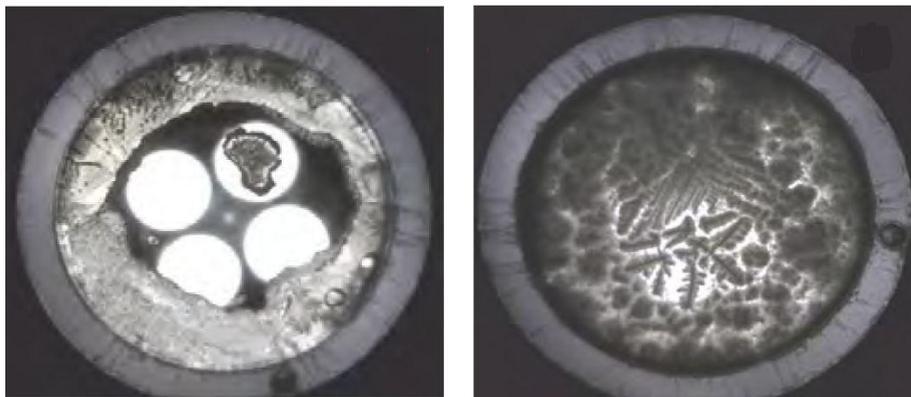
Initially, the influence of inhibitor was tested on LiCl only. These results indicated that ferrocyanide ions have no influence on LiCl nucleation and crystal morphology. Next, the influence of inhibitor was tested on a mixture of NaCl - LiCl. Three different salt concentrations were tested: 3 m NaCl -

1 m LiCl, 2 m NaCl - 2 m LiCl, and 1 m NaCl - 3 m LiCl. For all these experiments, 0.01 m inhibitor concentration was used. The results are shown in Figure 5. The solid lines are the expected paths to be followed upon drying of the droplet. As can be seen from the figure, the experimental data points coincide very well with the expected paths. The salt concentration first increases to the equilibrium line. At this point a salt crystal appears, as was confirmed from the pictures taken by the digital microscope. After the onset of crystallization the concentration of NaCl decreases and the equilibrium solubility line is followed, as shown by dotted arrows. These results show that multi-nuclear NMR is a powerful experimental tool to validate the phase diagrams.

For the mixture of NaCl - LiCl, no significant NaCl supersaturation was observed in the presence of inhibitor. These results indicate that in the presence of another salt, ferrocyanide ions are not able to supersaturate NaCl as highly as was seen in case of single salt. A higher supersaturation means a higher crystallization pressure; however, it must be kept in mind that calculating the crystallization pressure assuming ideal behavior can lead to significant errors. This is because the intermolecular interactions between liquids cannot be simply neglected. For example, in case of NaCl, for a given value of supersaturation e.g., 1.2, assuming ideal behavior the calculated value of  $P_c = 33.45$  MPa (calculated using eq.  $P_c = \nu RT/V_m \ln S$ ,  $C_{NaCl,o}$  is  $6.14 \text{ mol kg}^{-1}$  at 298.15 K,  $\nu = 2$  for NaCl,  $V_m = 27.02 \text{ cm}^3 \text{ mol}^{-1}$ ). However, including non-ideal behavior, the calculated value of crystallization pressure ( $P_c$ ) = 59.14 MPa, which is approx. 1.76 times higher than the one calculated assuming ideal behavior. A clear habit modification was also seen in the presence of inhibitor. The photos in Figure 6 show that more spreading occurred and dendritic crystals were formed in the presence of inhibitor.



**Figure 5:** The three tested concentrations of NaCl - LiCl mixtures shown in the ternary phase diagram of the NaCl - LiCl - H<sub>2</sub>O system. The open symbols denote salt mixtures with inhibitor and the closed symbols denote salt mixtures without inhibitor. The solid lines show the expected pathways to be followed before the equilibrium line is reached.



**Figure 6:** Images showing the crystal morphology at the end of a NaCl-LiCl drying experiment: (left) with no inhibitor (right) with 0.01 M inhibitor.

#### 4 Conclusions

The results show that ferrocyanide ions act as a strong nucleation inhibitor for NaCl when it is the only salt present. A significant higher NaCl supersaturation was observed in the presence of inhibitor and the supersaturation increases with increasing inhibitor concentration. For salt mixtures, it is found that the inhibitor will result in a lower supersaturation than that of the single salt. For both single salt and salt mixtures, the crystal morphology changes completely from bigger cubic crystals to dendritic crystals in the presence of inhibitor. The crystal size decreases significantly at high inhibitor concentrations.

This dendritic crystal morphology with immense spreading is seen for all the cases. In a porous material, this morphology can promote the formation of efflorescence that causes only little structural damage. The crystals formed in the presence of inhibitor were more powdery and fluffy and were easy to remove from the substrate. Consequently, the ferrocyanide ions may be beneficial for building materials that are contaminated with a salt mixture. Moreover, as the solution does not highly supersaturate in the presence of inhibitor, the risk of damage will be reduced.

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