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ELECTRONIC SUPPLEMENTARY INFORMATION

Brine rejection and hydrate formation upon freezing of NaCl aqueous solutions

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1. Concentration estimation

We have estimated the mass percent concentration from the MD simulations by counting the number of water molecules n_{H_2O} and ions n_{Na}, n_{Cl} within a given volume and using the corresponding molecular/atomic masses m_{Na}, m_{Cl} and m_{H_2O}:

$$c[m/m\%] = \frac{n_{Na} \cdot m_{Na} + n_{Cl} \cdot m_{Cl}}{n_{H_2O} \cdot m_{H_2O} + n_{Na} \cdot m_{Na} + n_{Cl} \cdot m_{Cl}}$$

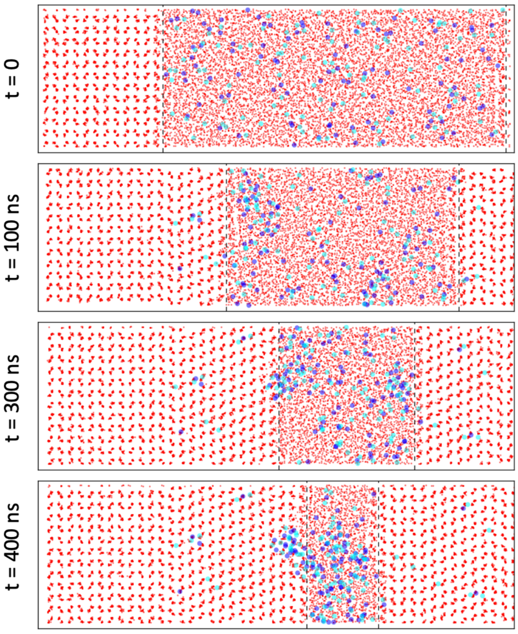

Fig. S1. Detail on the calculation of the concentration, where the dashed lines indicate values where the volume estimation.

Each frame was analysed separately and the volume of the brine was selected by taking vertical planes perpendicular to the ice growth axes, shown in Fig. S1. The straight boundaries were chosen due to simplicity, which seem to match pretty well the ice growth front.

In addition, we estimate the molar concentration, in the following way:

$$c[mol/L] = \frac{n_{Na} + n_{Cl}}{2 \cdot N_A \cdot V}$$

where N_A is the Avogadro number and V the volume. The molar concentration as a function of time is plotted in Fig. S2.

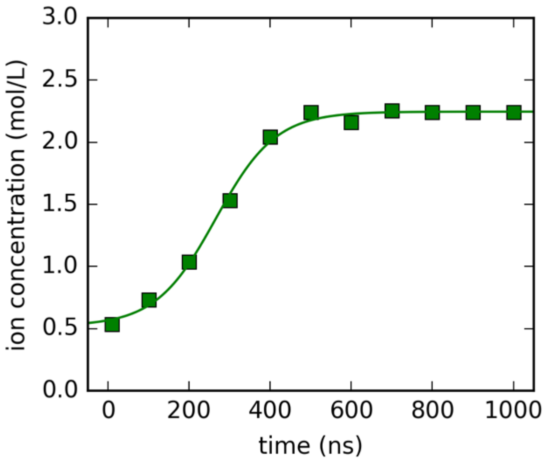

Fig. S2. The ion molar concentration of brine as a function of simulation time.

2. Cluster analysis

The cluster analysis was performed in the following way: we define a cluster consisting of ions that are linked with their first neighbor counterions, according to the ion coordination parameter. We kept only clusters consisting of more than 2 ions and in addition we merge neighbouring clusters, if their centers are separated by distances smaller than 10 Å. The last step assumes hierarchical clustering and the cut-off was selected by performing the analysis on a NaCl·2H_2O crystal, as detailed below. This step is necessary for identifying hydrate clusters due to the present of water molecules as part of the crystal.

The cluster analysis was tested the crystal dihydrate structure, shown in Fig.S3. The upper left panel shows the actual dihydrate structure. The cut-off values are indicated at the corresponding panels. The identified ion clusters are highlighted in different colours. One can see that upon increasing the cut-off parameter, eventually the whole crystal is identified as one cluster.

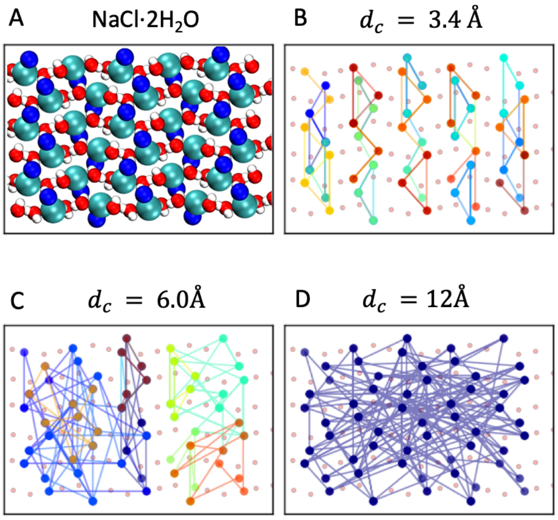

Fig. S3. Test of the clustering algorithm on a NaCl·2H_2O crystal. (A) the crystal, where the Na^+ ions are shown in blue, the Cl^- ions in cyan and the oxygens and hydrogens are shown in red and white. (B) The result from the cluster analysis applied on the crystals with a cut-off distance of 3.4Å. The different identified ion clusters are labelled with different colours. (C) and (D) The clustering analysis applied with cut-off distances 6.0 Å and 12 Å.

After identifying the appropriate values for the cut-off distance the clustering algorithm was applied on the MD trajectory. For each frame only the size and number of the largest cluster was identified. The results are shown in Fig. S4, where different frames are displayed with the identified ion clusters highlighted in colour. At early times only minor clusters are found (50 ns). As crystallization progresses and the brine concentration increases the average cluster size in progressively increases and finally peaks after 400 ns. We also show the number of molecules per cluster in Fig. S5, which follows the same trend with the cluster size shown in the main text.

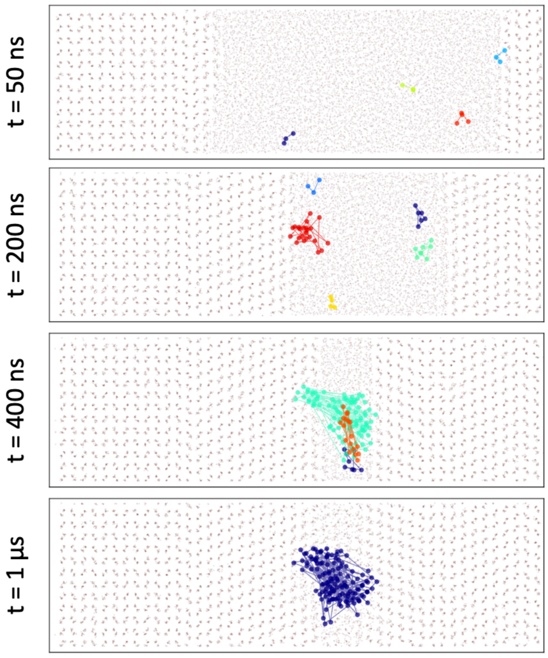

Fig. S4. Different frames from the cluster analysis applied on the MD trajectory. The simulation times are indicated in the right hand side and the corresponding identified ion clusters are highlighted in different colors.

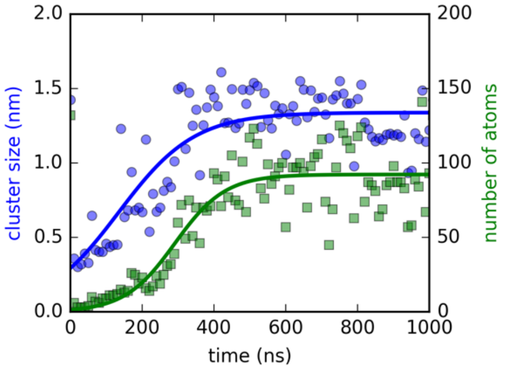

Fig. S5 The cluster size and the number of atoms per cluster as a function of time.

3. Hydrate radial distribution function

A $NaCl \cdot 2H_2O$ crystal was optimized with TIP4P and the radial distribution function was calculated in order to compare with the crystallite observed in the main text. The results are shown in Fig. S6. The peak at the O-Cl component (marked with a *) is also present in the MD simulation results presented in the main paper, which we consider a signature of the hydrate formation. This peak is not present in the corresponding liquid state or in the NaCl crystal.

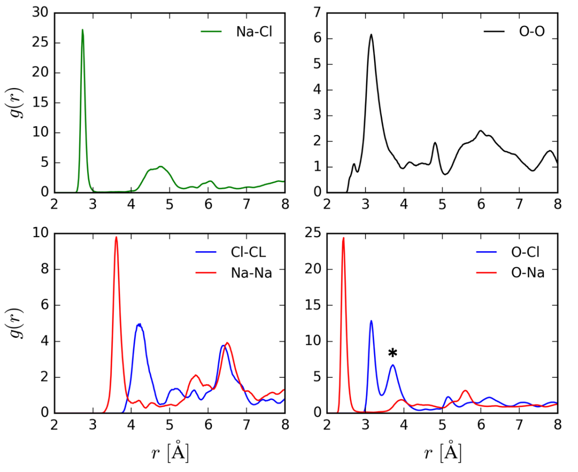

Fig. S6 The radial distribution function $g(r)$ obtained from a $NaCl \cdot 2H_2O$ crystal, which was optimized with TIP4P. The different panels correspond the different components, indicated in the legend. The (*) indicated on the O-Cl component is also indentified in the $g(r)$ presented in the main text, which is attributed to hydrate formation and is not present in the brine.

4. Hydrate scattering intensity

The diffraction pattern of NaCl dihydrate (Fig. S7) was modeled based on the refined structure determined by x-ray diffraction[1] (see inset Fig. S7). A Gaussian line shape with (FWHM) 0.05 Å^{-1} was used to model the contributions to the diffraction peaks from a convolution of the instrumental line broadening with the crystal size. In addition, the Debye-Waller factor DWF = $\exp(-BQ^2)$ was used in order to attenuate the peaks intensity due to thermal motion, where B is the fitting parameter for each temperature and concentration. The obtained diffraction pattern with (blue solid line) and without (black dashed line) the DWF (red solid line) is shown in Fig. S7 for a typical value of B = 0.4 Å^2.

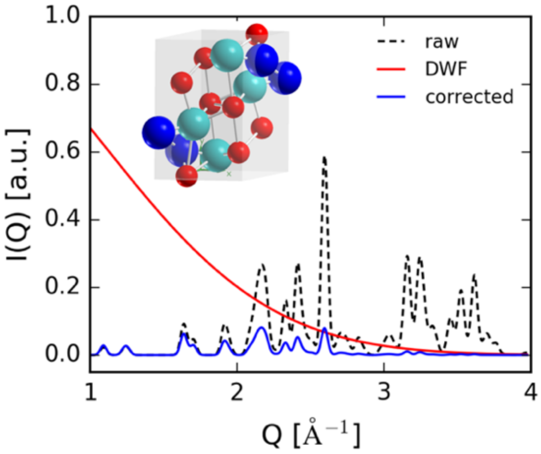

Fig. S7 The modelled XRD pattern of NaCl dihydrate obtained by structural refinement [1]. The Debye-Waller factor (DWF) is included to model the intensity attenuation due to thermal motion. The data obtained with (blue sold line) and without (black dashed line) the DWF are shown here. The inset depicts the structure of the $NaCl \cdot 2H_2O$ hydrate, where O atoms are represented by red spheres, Na^+ ions by dark blue, Cl^- ions by turquoise spheres and H atoms are not shown.

References

1 B. Klewe and B. Pedersen, The crystal structure of sodium chloride dihydrate, *Acta Cryst B*, 1974, **30**, 2363–2371.