

Supplementary Materials for Salt creeping as a self-amplifying crystallization process

M. J. Qazi, H. Salim, C. A. W. Doorman, E. Jambon-Puillet, N. Shahidzadeh*

*Corresponding author. Email: n.shahidzadeh@uva.nl

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Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/5/12/eaax1853/DC1)

Movie S1 (.avi format). NaCl solution—Zoom at the contact line.

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Movie S3 (.avi format). Na_2SO_4 -B—General view of salt creeping of the anhydrous sodium sulfate (thenardite).

Supplementary Materials and Methods

Preparation of salt solutions

Homogeneous salt solutions, i.e. without crystal seeds, were prepared by dissolving salts in Millipore water ($\rho \sim 18.2 \text{ M}\Omega\cdot\text{cm}$) at concentrations slightly under saturation; i.e. relative supersaturation $S = m_i/m_s = 0.9$, with m_i the initial concentration and m_s the saturation concentration. Details about the materials are provided in table S1.

To control the precipitation of either the hydrated form (mirabilite) or the anhydrous one (thenardite) of sodium sulfate during the experiment, undersaturated salt solutions were prepared based on the equilibrium phase diagram of sodium sulfate at either 21°C ($\text{Na}_2\text{SO}_4\text{-A}$) or 35°C ($\text{Na}_2\text{SO}_4\text{-B}$). For the latter, the solution is kept at 35°C by heating up the petri dish throughout the creep experiment.

The solutions were used 24 hours after preparation. The surface tensions of the different solutions were measured using a Krüss Instrument (table S1).

Table S1. Properties of the salt solutions studied.

Salt	T of the reservoir ($^\circ\text{C}$)	m_s^* (molal= mol/kg)	ρ_s (g/cm^3)	γ (mN/m)	Interface where crystallization takes place	Purchased from
$\text{Na}_2\text{SO}_4\text{-A}$ (mirabilite)	21	1.35	1.19	76.1	Liquid/air	Prepared from anhydrous form
$\text{Na}_2\text{SO}_4\text{-B}$ (thenardite)	35	3.5	1.29	78.5	Solid/liquid	Sigma Aldrich (Purity $\geq 99\%$)
KCl	21	4.56	1.15	78	Liquid/air	Sigma Aldrich (Purity $\geq 99\%$)
NaCl	21	6.14	1.2	81.4	Liquid/air	Sigma Aldrich Purity 99%

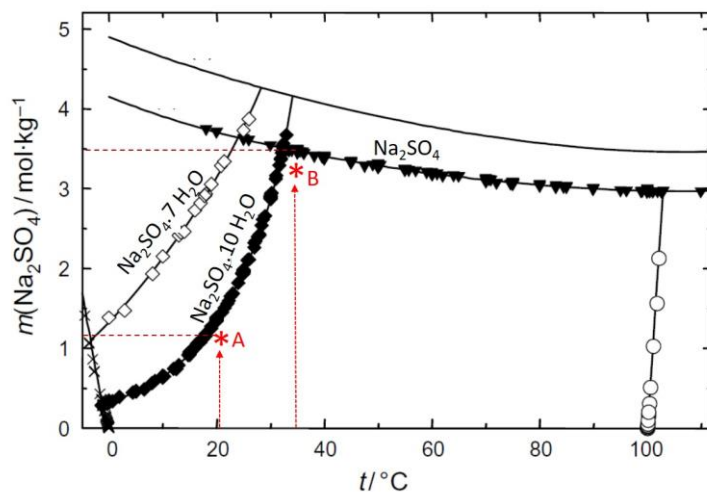


Fig. S1. Phase diagram of Na_2SO_4 in water as a function of temperature (9). Points A and B refer to the initial understaturated salt solutions at $S=m_i/m_s=0.9$ prepared for this study to promote the precipitation of the hydrated form $\text{Na}_2\text{SO}_4\text{-A}$ or the anhydrous phase of sodium sulfate $\text{Na}_2\text{SO}_4\text{-B}$.

Preparation of NaCl and Surfactant solutions

To study the impact of surfactants on NaCl creep, aqueous surfactant solutions were prepared at their critical micelle concentration (CMC): for the cationic surfactant CTAB (from Sigma Aldrich; 99.8% purity), this concentration was 0.9 mM; for the non-ionic surfactant Tween 80 (obtained from Amreco Ltd) 0.015 mM. Subsequently, in both cases, the surfactant-salt solutions were made by adding NaCl at concentration $S = m_i/m_s = 0.9$ to the previously prepared surfactant solutions.

Figure S2 shows bulk crystallization with evaporation of NaCl with and without additives CTAB and Tween 80. The addition of CTAB causes the crystallization of multiple nuclei - more than formed in pure NaCl. The addition of Tween 80 results in the formation of only a single large crystal. The surfactants therefore allow to control the number and the size of the crystals formed.

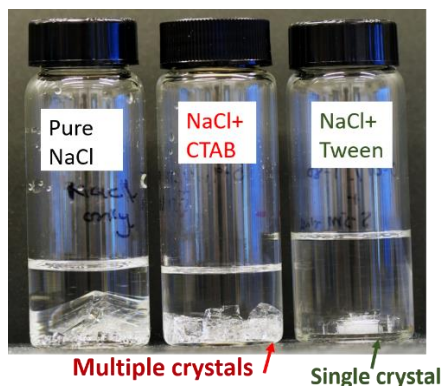


Fig. S2. Influence of surfactants CTAB and Tween 80 (CMC concentrations) on the nucleation of NaCl in the bulk at RH=40% and T=21°C.

We also characterized the wetting properties of a droplet of NaCl solution and of a NaCl-surfactant solution on a horizontal glass surface. As shown in the fig. S3, despite a significant decrease in the surface tension (from 81mN/m to 40mN/m), there is only a minor change in the contact angle of the NaCl solution in the presence of the Tween 80. In case of CTAB, again, there is a major change in the surface tension of the solution (from 81 mN/m to 32 mN/m), but the contact angle increases from 25 (pure NaCl) to 32 (NaCl/CTAB) degrees. From Young's principle, it would be expected that the contact angle decreases as the surface tension decreases. However, that does not seem to be the case for the two surfactants when added to a high salt concentration. The increase in the contact angle in the presence of the CTAB has been explained in earlier studies to be due to adsorption of the positively charged CTAB molecules on the negatively charged glass surface, causing an autophobic effect (25). For Tween 80, it appears that the high electrolyte concentration also facilitates the adsorption of Tween 80 molecules to the glass surface (21).

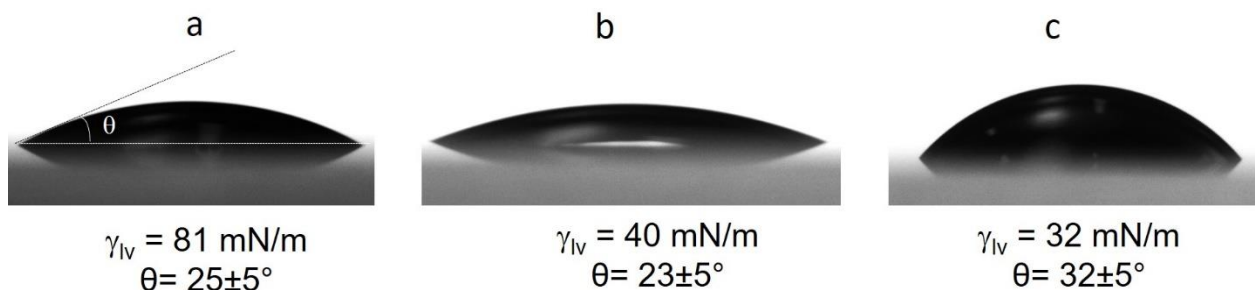


Fig. S3. Influence of the surfactants on the wetting properties. Contact angle of (a) 5.5m NaCl, (b) 5.5m NaCl+Tween 80, and (c) 5.5m NaCl+CTAB solution on a very cleaned glass surface . The concentration of surfactants is at their cmc.

Experimental setup of vertical creeping

The creeping experiments were performed using a custom-made setup consisting of a hydrophilic substrate (a smooth cylindrical glass rod to avoid effects of corners or roughness) suspended to a mass balance (fig. S4) which records the rod's mass at 2-minute intervals. The (initially undersaturated) salt solutions (table S1) were poured into a Petri dish and placed on an adjustable stage which is carefully moved upwards till the substrate comes in contact with the surface of the liquid due to capillary forces, forming a concave solution meniscus with the substrate. The whole setup is enclosed in a climatic chamber in which the relative humidity is precisely controlled. All the evaporation experiments were performed at room temperature (21°C). The time evolution of the meniscus was recorded with one camera while the initiation and growth of salt creep was recorded from further away with a another one. The images of either camera were taken at intervals of 5 minutes. The contact angle of the solution with the substrate was determined from these images using ImageJ software.

For each salt solution, experiments were conducted at least 5 to 6 times in order to ensure the reproducibility of the results. More than 60 experiments were performed at both low (6%) and high (40%) relative humidities.

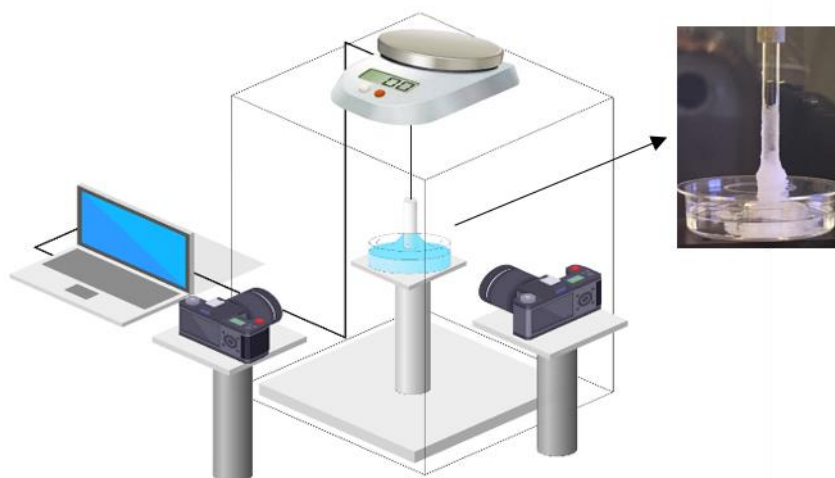


Fig. S4. Experimental setup. Left : schematic of the setup used to perform the creeping experiments. Right: zoom on the creeping experiment (here KCl solution). The diameter of the glass rod is 6 mm.

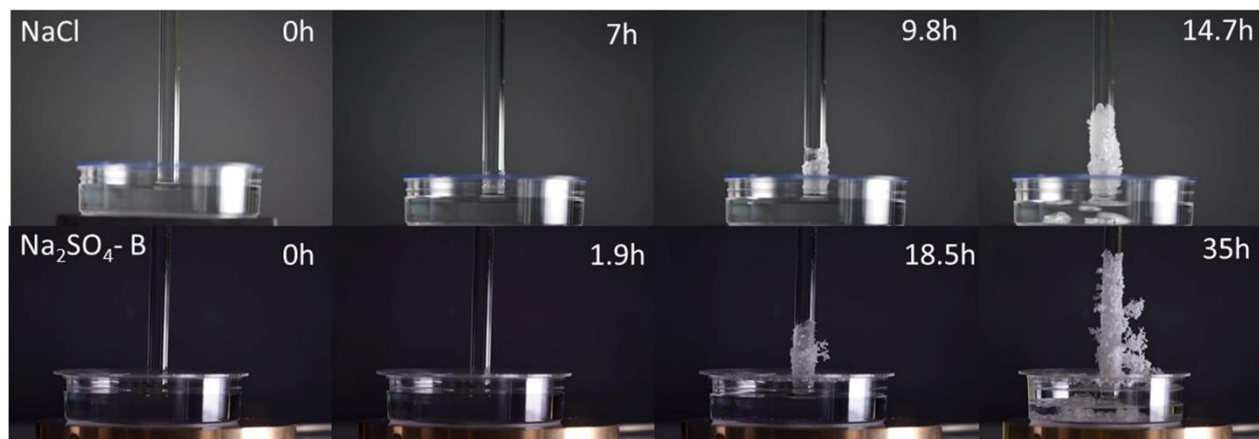


Fig. S5. Initiation and growth of salt creeping during the evaporation. Time lapse images for 2 different salt solutions NaCl and Na₂SO₄-B which leads to the precipitation of the anhydrous sodium sulfate crystals. (T~21°C, RH ~6%).

1. Contact line dynamics

We measured the position of the contact line at different time intervals. We found that the contact line remains pinned in the beginning of the experiment and detaches roughly with the first crystals nucleation in the solution. The crystal nucleation seems to triggers depinning of the contact line and from that point onwards there is no significant change in the evolution of contact angle. Fig. S5 shows the position of the contact line in a photograph taken early in a typical experiment, and change in height thereof with respect to the initial position as a function of time.

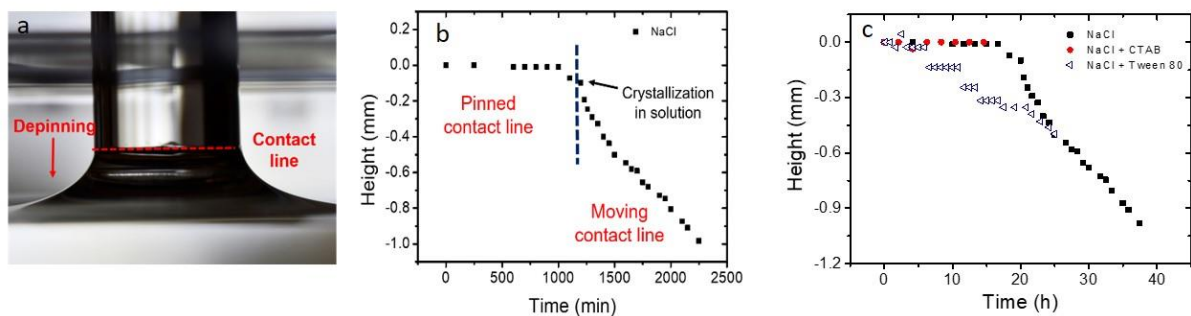


Fig. S6. Evolution of the contact line. (a) Photograph of the salt solution's meniscus wetting the glass rod early in a typical experiment. The contact line (indicated by the dashed red line) is pinned initially. As the experiment progresses, the meniscus moves downwards (red arrow) and eventually the contact line gets depinned. (b) Graph of the lowering of the contact line with respect to its initial height as function of time for a NaCl solution evaporating. (c) As (b), also including NaCl solutions to which surfactants CTAB and Tween 80 were added.

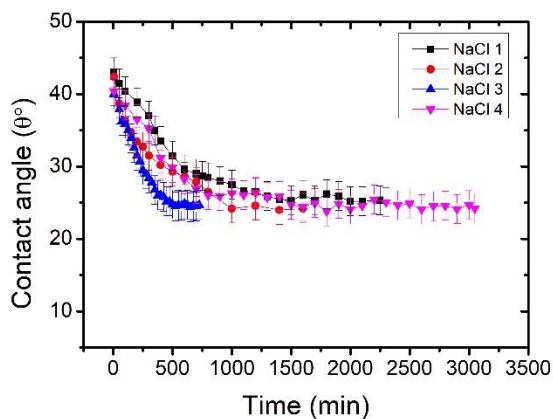


Fig. S7. Evolution of the contact angle up to creeping. Results of four experiments on the same NaCl solution showing the reproducibility of the measurements (RH=6%, T=21°C)

In addition, we have performed some new creeping experiments on the glass rod with half the diameter (3 mm) compared to the rod used in studies presented in the manuscript. We found once again that (1) the creeping does take place and (2) the critical contact angle is the same to within the experimental uncertainty (Fig. 3) as for the rod with the larger diameter.

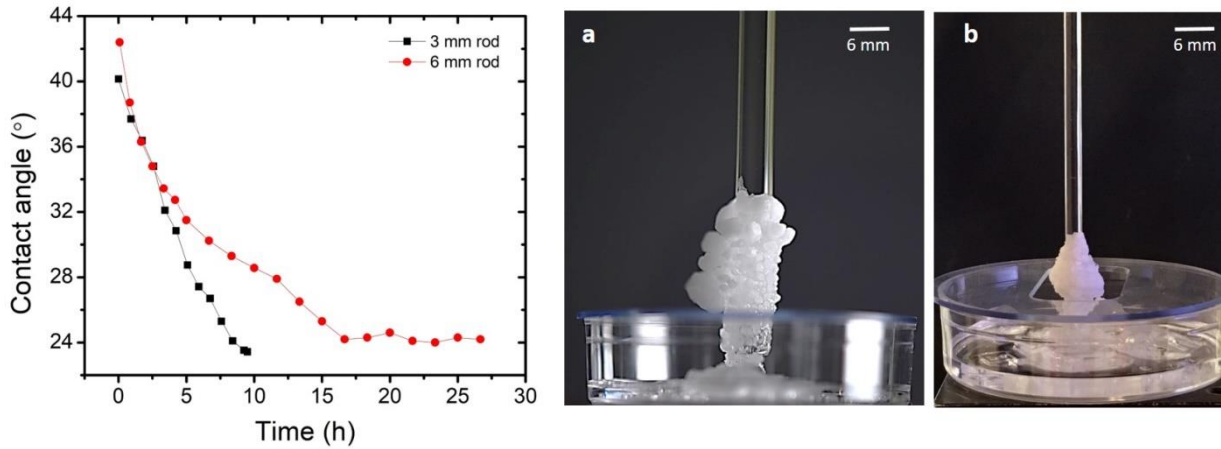


Fig. S8. Effect of the curvature of the glass rod. Left: Evolution of the contact angle with time for the creeping experiment with NaCl solutions on glass rods with the diameter of 3 mm and 6 mm (creeping starts at the last data point). Right: comparison of the creeping at the end of experiments for the two substrates (a) $d=6\text{mm}$, (b) $d=3\text{ mm}$.

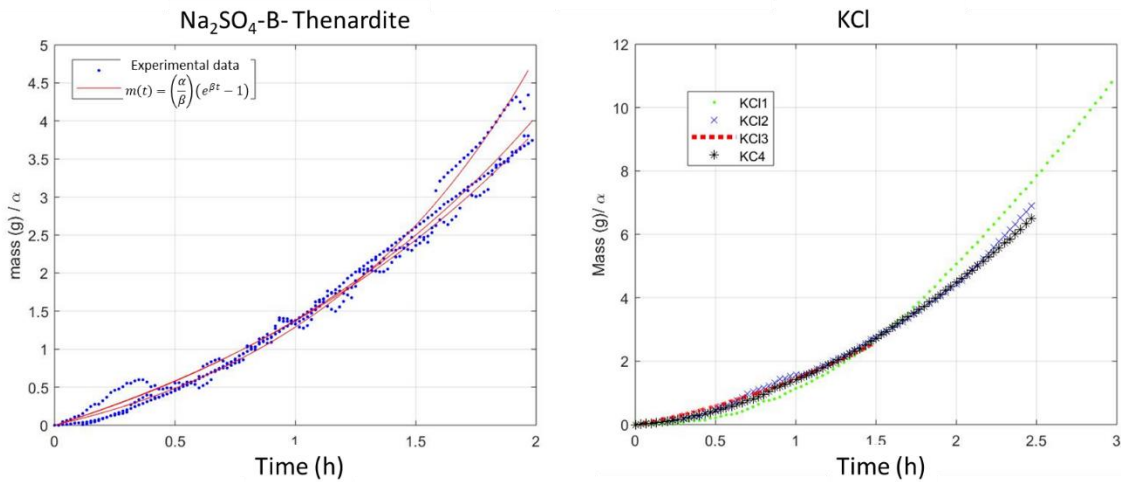


Fig. S9. Mass of the salt creep (normalized). Left : Results for three different $\text{Na}_2\text{SO}_4\text{-B}$ experiments showing the reproducibility of the results. Right : Results for 4 different KCL experiments.

3- Creeping on flat surfaces

The creeping phenomenon is very generic; it can be seen on many buildings, for instance. In our setup, it also happens on flat surfaces, as can be seen below. Therefore, the phenomenon is independent of the effect of curvature as the same critical contact angles were observed for the flat glass slides also (figure S10).

Initially we started doing our experiments using such glass slides. The results show that the creeping starts at the same contact angle as on the cylindrical substrate (figure S11). However, the roughness of the edges and the corners of the glass slide can also act as preferential creeping locations because they are rough. To avoid this in our experiments on flat glass slides, the edges were treated with hydrophobic treatment in the example shown below.

Therefore, in order to make the entire surface homogeneous and demonstrate the role of the critical contact angle for different salts as clearly as possible, the quantitative experiments in the paper were done with smooth glass cylinders. Figure S11 below shows the measured evolution of the contact angle on the flat surface.

The reason for the non-existence of the effect of the curvature being that the initiation of creeping is determined primarily by the confinement of nucleated crystal between the substrate and the meniscus.

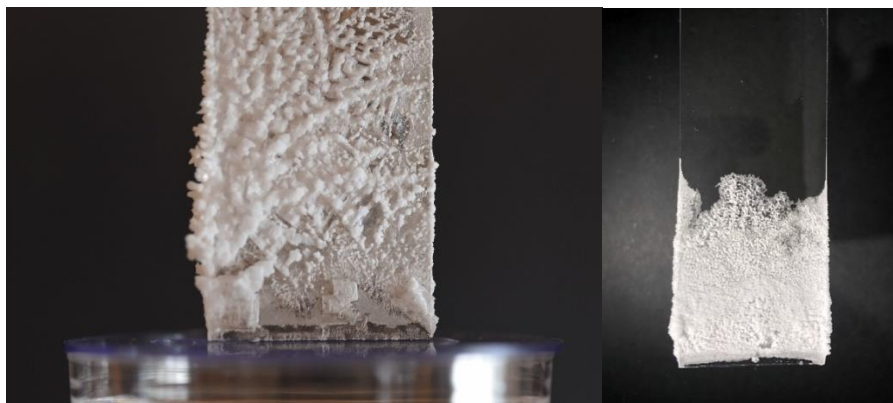


Fig. S10. Experiment of creeping of NaCl and Na₂SO₄ on the glass slide.

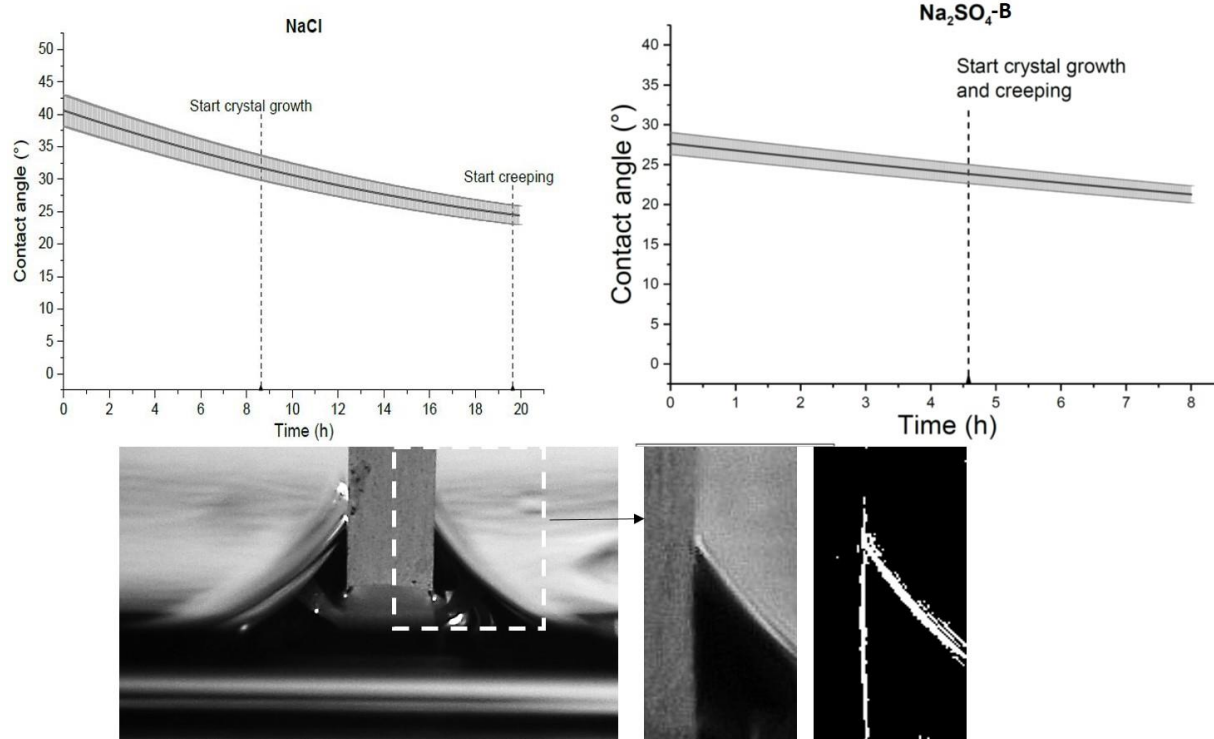


Fig. S11. Salts creeping on glass slide. Top: Evolution of contact angle with evaporation time on glass slide up to the initiation of creeping for NaCl and Na₂SO₄-B. The same range of critical contact angles are reached as for cylindrical glass substrates. Bottom: The contact angles are determined by image analysis of the contact line profiles. The edges of the glass slides were treated with a hydrophobic treatment to avoid crystal nucleation due to the roughness of this region.

Movie S1. NaCl solution—Zoom at the contact line.

Movie S2. NaCl + CTAB solution—General view of salt creeping.

Movie S3. Na₂SO₄-B—General view of salt creeping of the anhydrous sodium sulfate (thenardite).