Further steps towards the solution of Correns' dilemma

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Abstract

Correns' and Steinborn's pioneering experiment is probably the most intriguing one in the field of salt crystallization. It consisted of the measurement of the force needed to prevent a monocrystal of potassium alum (potassium and aluminium sulfate dodecahydrate, $KAl(SO_4)_2 \cdot 12\ H_2O$) from growing in various supersaturated solutions. What is puzzling is that they obtained very good agreement between their experimental data and an ideal equation of crystallization pressure.

We report here the experimental advances in our modern reproduction of this milestone experiment. We developed a setup that includes a universal testing machine, custom-made glassware, and an external stirring system. Here, we present and comment on the data derived from the first 11 experiments. We found that many aspects of the work by Correns and his collaborators should be put into question, along with a thorough analysis of the non-ideal thermodynamics of potassium alum. Slowly, we are getting closer to answering the mystery that continues to surround this experiment.

Keywords: crystallization pressure, potassium alum, supersaturation, thermodynamics

1   Introduction

Crystallization of salts from aqueous solutions is an important weathering phenomenon of porous building materials and concerns different fields of studies. The underlying thermodynamics, kinetics, and mechanics have been extensively studied, and it is now well established how the resulting crystallization pressure can cause significant stresses and, therefore, damage [1–9]. However, quantitative data are still relatively rare to find in literature [10–15].

Correns and Steinborn derived the first equation for crystallization pressure in their paper in 1939 [11,16] (a subsequent and much more succinct paper in English with Correns as the only author was published in 1949 [12,16]):

$$P = RT/v \ln(c/c_s) \tag{1}$$

In (1), P is the crystallization pressure, R is the gas constant, T is the temperature, v is the molar volume of the solute, c is the actual concentration, and c_s is the saturation concentration at T. The system studied by Correns was potassium alum (potassium and aluminium sulfate dodecahydrate, $KAl(SO_4)_2 \cdot 12\ H_2O$), probably because of its low cost, easy availability, relative stability of the supersaturated solutions, and ease of obtaining good single crystals [17]. With his ingenious pressure balance (*Druckwaage* in German), Correns observed growth or no growth of a potassium alum single crystal in its supersaturated solution, when loaded below or above the value of pressure resulting from (1), respectively [11,12,16].

The results in Correns' papers show an excellent agreement between the experimental data and (1). However, the latter equation is – at best – incomplete because it neglects the non-ideal behaviour of concentrated solutions of electrolytes [16]. In fact, the correct version of (1) for large crystals is:

$$P = RT/v \ln(Q/K) \tag{2}$$

where Q is the ion activity product and K is the solubility product, the other symbols are the same as in (1).

Furthermore, in both Correns' papers [11,12,16] relatively few experimental details are given; some more are present in the work by Brehler (one of Correns' doctoral students [18]) but several doubts about the validity of his findings persist.

Correns' work remains however pioneering for what concerns his identification of the role of surface energies. In fact, he showed that growth is observed at different extents if the surfaces between which the crystal is loaded are made of materials other than glass, or if the crystal is differently oriented.

This paper extensively illustrates the method for obtaining and characterising potassium alum crystals, and the setup used to measure the thickness of potassium alum crystals after their (111)-faces loading in supersaturated solutions between glass surfaces. We present and comment also some first measurements at low supersaturations (1.10 and 1.15), so to neglect the role of the different surface energies of the faces of the crystals.

The contents of this paper questions aspects of the work by Correns and his collaborators, others than the ones already discussed by Flatt *et al.* in their commented translation of the 1939 paper [16]. This work follows a preliminary one in which potassium alum supersaturated solutions were characterized [17].

2 Experimental

2.1 Instrument

The application of a constant load and the measurement of the displacement were performed on a 10 kN universal testing machine 1454 by Zwick GmbH (Ulm, Germany). The employed load cell was a high precision 1 kN one. The load is applied through a custom-made aluminum pushrod, previously described in [17]. The load application rate is 5 N/min. The machine keeps a constant load by continuously adjusting the position of its traverse. Therefore, it does not allow a direct and continuous recording of a possible displacement of the crystal.

The nominal resolution of the machine is 0.2 μm. The program used for the acquisition of data was TestXpert II by Zwick.

2.2 Glassware

For the purpose of the experiment, we designed crystallizing dishes and glass sockets with flat faces and thus parallel to the potassium alum single crystals. A specialized glassblower (Comandè Saskia, Monreale, Italy) produced the pieces of glassware. The crystallizing dish has a diameter of 10 cm and a height of 5 cm for containing a volume of around 400 mL of solution. The socket has a diameter of around 2.3 cm and a height of 5.5 cm. The socket is designed to completely cover the face of the crystal under load [16].

Before the use in the experiments, all the glassware has been carefully washed and dried in a laboratory dishwasher, using only demineralised water.

Both the crystallizing dish and the socket are shown in Figure 1, left.
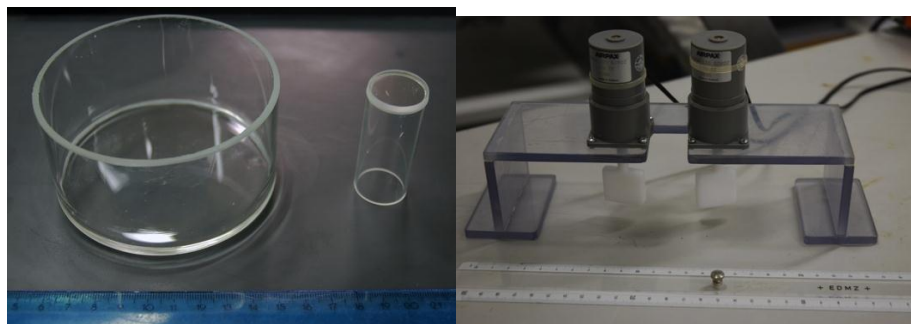
Figure 1: The custom-designed borosilicate glass crystallizing dish and socket (left) and the custom-made powered stirring system with poly(methylene oxide) pads (right) used for the experiments.

2.3 Potassium alum supersaturated solutions and crystals

Supersaturated solutions were prepared (and stored) in borosilicate glass bottles with screw caps by stirring and heating ultrapure water (UPW) and analytical grade potassium alum from either Merck KGaA (Damstadt, Germany) or Sigma-Aldrich Chemie GmbH (Buchs, Switzerland).

The refractive index of such solutions was measured with a pocket refractometer PAL-RI by Atago (Tokyo, Japan), after performing the zero setting with UPW.

The solubility value of potassium alum (5.9 g/100 g water at 20 °C for the anhydrous salt, corresponding to a solubility of 11.4 g/100 g water for the dodecahydrate at the same temperature) is taken from the literature [19].

Single crystals were obtained by cooling down supersaturated potassium alum solutions (with a concentration of around 13.1 g/100 g water) from 20 °C to 5 °C in a Vötsch VC 4060 climatic chamber (Vötsch Industrietechnik GmbH, Balingen-Frommern, Germany) in the above-described crystallizing dishes covered with a Petri dish. The cooling rate was 1 °C/h. Under these conditions, around 1 day is necessary for the potassium alum to nucleate and crystallize. Only crystals with a good overall aspect (absence of cracking and asperities on the surface) and not twinned to others were chosen. A micrograph of a typical crystal is shown in Figure 2.
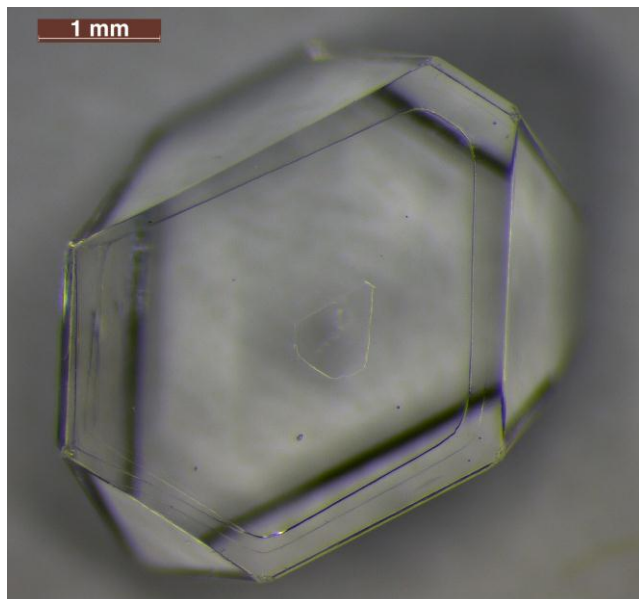
Figure 2: Micrograph of a potassium alum single crystal oriented on the (111) face.

The masses of the crystals were recorded with a Mettler-Toledo NewClassic MS-204S analytical balance (Mettler-Toledo GmbH, Greifensee, Switzerland).

All the crystals were then observed under an M60 stereomicroscope by Leica Microsystem AG (Heerbrugg, Switzerland). Micrographs at different magnification were taken using the LAS program by Leica.

The values of the (111) surface areas were obtained by analysing the above-mentioned micrographs with the image-processing program ImageJ 1.47v, created by Wayne Rasband (National Institutes of Health, USA).

The measurement of the thickness of the crystal – before and after the experiment – was carried out as follows: i) the crystal is put at the centre of the crystallizing dish; ii) the machine applies a 5 N load on the crystal through the pushrod (without the glass socket) at a rate of 5 N/min; iii) the height of the pushrod on the crystal is recorded when the machine reaches such load. This procedure allows a precise (the standard deviation on 5 replicates is, generally, around 1-2 μm, and ranged from < 1 μm to around 20 μm in the experiments reported in this work) and reproducible value of the thickness of the crystals.

2.4 Stirring system and other experimental parameters

A powered stirring system (Figure 1, right) with poly(methylene oxide) pads was designed and built in house. When the stirring system was not employed, a glass rod was then used.

A sponge pad – kept wet with ultrapure water – was used on the edges of the crystallizing dish to ensure minimum evaporation of the solutions.

All the experiments were carried out in a climatic room at constant temperature (20 °C ± 2 °C) and relative humidity (50% ± 8%).

11 experiments (Figure 3) were carried out with solutions at supersaturation either 1.10 or 1.15. The applied load ranged from the crystallization pressure predicted by (1) to 1.9 times it.
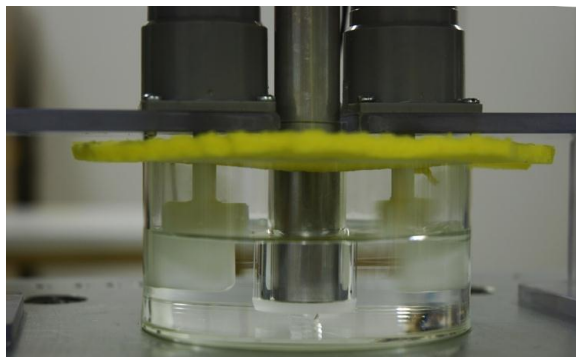
Figure 3: A close-up of a running experiment. The crystallizing dish, the glass socket, the aluminium pushrod, the powered stirrer, and the potassium alum crystal are visible.

3 Results and discussion

A table showing the relevant data and the outcome of the experiment is here reported (Table 1).

Table 1: Outcome of the 11 experiments discussed in this paper. "c/c_s" stands for supersaturation and it refers at that value at 20 °C. The applied load is expressed as a multiple of the crystallization pressure resulting from (1). The thickness of the crystal after the loading in the supersaturated solution is reported in the "Outcome" column. The "Surface" refers to the mean value of surface area of the two (111) faces of the potassium alum crystal. The standard deviation of the thickness of the crystal is given in parenthesis.

ID	Surface (mm²)	Mass (mg)	c/c_s	Load ($P_{Correns}$-fold)	Thickness (mm)	Duration	Outcome
1	21.2	148.2	1.15	1.45	3.921(0)	12 h 25'	Not grown (3.89(2) mm) and broken
2	55	317.2	1.10	1.45	4.031(0)	14 h 30'	Not grown (4.028(3) mm))
3	58	211.7	1.15	1	3.068(1)	---	Broken during exp.
4	9.8	13.2	1.15	1	1.183(5)	20 h 30'	Not grown (1.18(1) mm)
5	10	21.2	1.10	1	1.533(0)	1 h	Not grown (1.513(1) mm)
6	13	22.1	1.10	1	1.342(1)	1 h 40'	Grown (1.394(1) mm)
7	12	25.4	1.10	1.9	1.444(0)	40'	Not grown (1.431(1) mm)
8	5.3	8.6	---	---	---	---	Broken during thickness meas.
9	9	16.1	1.10	1	1.343(0)	2 h 5'	Not grown (1.337(1) mm) and broken
10	16	31.8	1.10	1	1.505(0)	45'	Not grown (1.476(1) mm) and broken
11	10	19.8	1.10	1.52	1.452(0)	1 h 50'	Not grown (1.449(1) mm) and broken

For experiments 1-3, we employed bigger crystals than the ones used after. Correns did not report any information about the dimension of the employed crystals [11,12,16] but Brehler did [18] and referred to quite small crystals (similar in dimensions to the ones reported in this study). The use of large crystals means higher probability of defects and a corresponding higher probability of breakage of the crystal during the loading phase. However, Brehler fails to indicate how he obtained the values of the surface areas of the crystal faces, despite being precise to the mm^2 [18]. An accurate value is critical for the calculation of the load to be applied.

In 6 experiments out of 11, the crystal broke either after the loading or during the measurement of the thickness. Such a frequent occurrence of breakage may be attributed to three factors: i) an intrinsic fragility of the crystals when under load; ii) the presence of defects in the crystals; iii) the dynamic application of the load by the machine. Excluding the last factor, this evidence questions the possibility of carrying out experiments at supersaturations (and, therefore, loads) higher than the ones reported in this work.

From Table 1, it can be noted that experiments 1, 2, and 4 had higher duration than the others. In fact, from experiment 5 on, when the first crystal appeared (nucleated) on the bottom of the crystallizing dish, the experiment was interrupted. It is worth remembering that when two crystals are immersed in a supersaturated solution and one of them is loaded, the unloaded crystal will grow at the expense of the loaded one.

The external powered stirrer was a cause of disturbance to the system and enhanced nucleation. Correns – probably aware of the concentration gradient that would result if the solution during the experiment were unstirred – reported that the solutions were stirred [11,12,16]. Considering that he did not describe any automatic stirring system and that the experiments were rather long (up to a couple of days), it is hard to imagine that: i) continuous stirring of the solutions (probably, by hand with a glass rod) during the experiments was performed; ii) nucleation (especially at high supersaturations) did not occur.

Only experiment no. 6 showed a growth of the crystal. This experiment indicates that the calculated value of the potassium alum crystallization pressure by Flatt *et al.* [16] is probably overestimated. It also suggests that other treatment of the activity coefficients may be needed for this system. Buil [10] reports that taking this into account resolves the discrepancy, but his work was never published. A more detailed consideration of the non-ideal solution thermodynamics of supersaturated potassium alum solutions however appears necessary in addition to the continuation of our experiments.

4   Conclusions and outlook

We presented a setup designed to carry out experiments of constant loading of potassium alum single crystals immersed in supersaturated solutions. We also presented a robust (albeit not continuous) method to measure the thickness of the single crystal before and after the loading in its supersaturated solution.

From the first results we obtained, we put into question further aspects of the work by Correns and his collaborators: the dimension of the potassium alum crystals, the stirring, and the resulting stability of the solutions (especially at high values of supersaturations). Furthermore, considering the shape of the chosen crystals, it is not clear how Correns and collaborators could have carried out loading experiments on faces others than the (111).

We will continue performing experiments at different loads to verify if further improvements to our setup are necessary or if the load range we are working on is correct.

For the future, a continuous recording of the movements of the crystal when loaded would be desirable. A custom-made accessory for the pushrod for mounting three independent displacement transducers on it has already been designed and produced. The implementation for the transducer is under development.

Finally, our still preliminary results suggest that the non-ideal solution thermodynamics of potassium alum supersaturated solutions may have to be re-examined.

Acknowledgments

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