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From the Research Laboratories

INVESTIGATING THE PARAMETERS WHICH INFLUENCE THE LENGTH AND SHAPE OF MGSO$_4$ CRYSTALS

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Abstract. The purpose of this paper is investigating and varying parameters which influence the length and shape of $MgSO_4$ crystals, obtained from solution. The manuscript discusses the theoretical model of the crystallization and approximations used; the parameters investigated- temperature of preparing the saturated solution, using different solvents (methanol, ethanol, acetic acid, and their mixtures with water) and the effect of the surface; the procedure for measuring the crystals. Crystal length is expected to be inversely proportional to the temperature of preparing the solution because of the increase in the nucleation rate in relation to the temperature; inversely proportional to the vapor pressure of the solvent used, because of the direct relation between vapor pressure and time period for crystal growth; and directly proportional to the solubility of $MgSO_4$ in a particular solvent. The validity of these expectations will be proved in this paper using the results, obtained from the conducted experiments. Results and conclusions are highlighted.

Keywords: Magnesium sulfate; crystals; length; temperature; solvents

Theoretical model

The main phenomena, which have a relationship with the length and size of the crystals, are the nucleation rate (Myerson & Trout 2013) and the level of supersaturation (Helt 1976). The rate of nucleation determines the number of nuclei, around which crystals are formed. The increase in the temperature leads to an increased nucleation rate which leads to more nuclei, leading to a greater number of crystals. This effect leaves less amount of salt per individual crystal. The level of supersaturation is proportional directly to the temperature of preparing the solution. Both phenomena are also dependent on the solubility of the salt, which can be varied by using different solvents. The rate of evaporation determines the time for crystal formation. It could also be varied by using different solvents, because of their difference in vapor pressure. The exact relation of these factors, as well as their overall importance to the effect, will be revealed using the results from the experiments.

Most of the experiments were conducted using $MgSO_4$, the heptahydrate form for investigating preparation temperature of the solution as a factor, and anhydrous for the rest of the experiments. The choice of this particular inorganic salt can be reasoned, providing that for calculating concentration of the solute in a solution of non-water solvent, the amount of water from the crystal has to be calculated, if hydrated salt is used. This can be avoided by using a relatively stable anhydrous salt, which is characteristic for magnesium sulfate. Another advantage of using $MgSO_4$ is the long crystal it forms, which can be observed in detail more easily than other salts crystals.

When collecting quantitative data about crystallization, it is worth noting that crystal formation is a complex process, influenced by random factors. This leads to differences between the different samples, even under the same controlled conditions. The main purpose of this paper is to investigate the relation between different parameters. In order to achieve this, some of the quantitative data has been approximated, usually by using average length of the crystals, the value of which, although not absolutely precise, can be used for the purpose of the study.

Measuring the crystals

The main measurement taken of the crystals is their average length. It is calculated by measuring the length of 30 random crystals (Fig. 1a) using sophisticated software for the choice and measuring the length. For measuring smaller crystals, microscopic images (Fig. 1b) were used for higher accuracy.

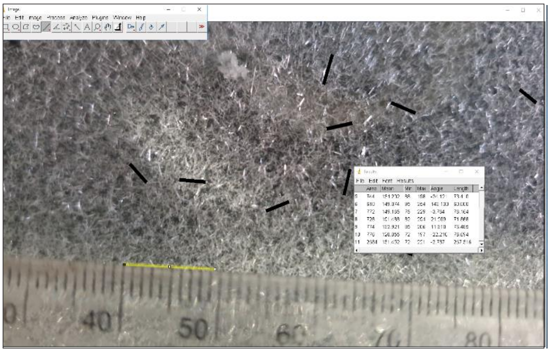

Figure 1a. Crystal measurements

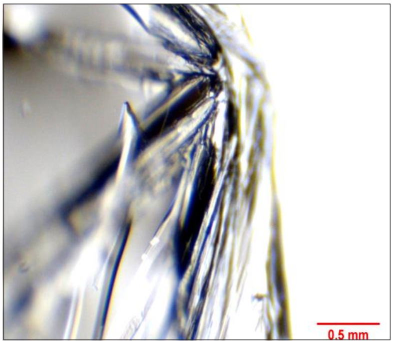

Figure 1b. Microscopic images

Experimental setup

All of the following experiments were conducted in a controlled environment, with monitoring of temperature and atmospheric pressure, as both conditions may affect the results, because of their relationship with nucleation rate and vapor pressure. For the experiment related to the temperature of preparing the solution, thermostat with magnetic stirrer (Fig. 2) was used to ensure adequate temperature control and dissolving of the solute. For the experiment related to the use of different solvents, only magnetic stirrer was used, because the temperature of the solvents was intended to be at room temperature, because of the volatility of some of the solvents used. The main glass vessel used for growing the crystals is 10cm Petri dish. However, the use of different type or size of vessel did not cause notable deviation in the results, except the vessels with diameter equal to or less than 5cm.

Figure 2. Experimental setup

Temperature

Purpose of the experiment: To obtain quantitative data about the relationship between temperature of preparation of the solution and the length of the crystals.

Setup: Supersaturated aqueous solutions of $MgSO_4.7H_2O$ are prepared at different temperatures of the solution using a thermostat. Crystals are measured after all of the water has evaporated. The crystals were grown in Petri dishes, 10 cm in diameter each.

Results:

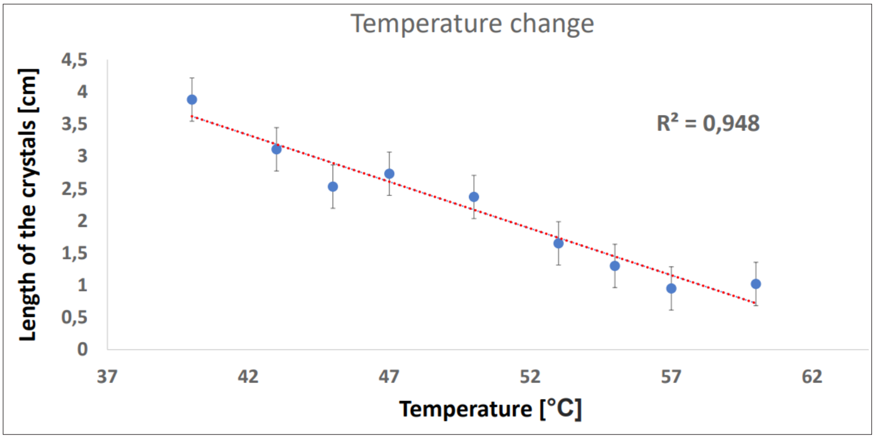

Figure 3. Temperature influence chart

The graph shows the average length of the crystals depending on the temperature of formation of the solution. The linearity of the graph (Fig. 3) can be explained using the fact that the solubility of magnesium sulfate is also linear within this temperature range (Krumgalz 2018). It, therefore, shows the importance of solubility as a factor in crystallization.

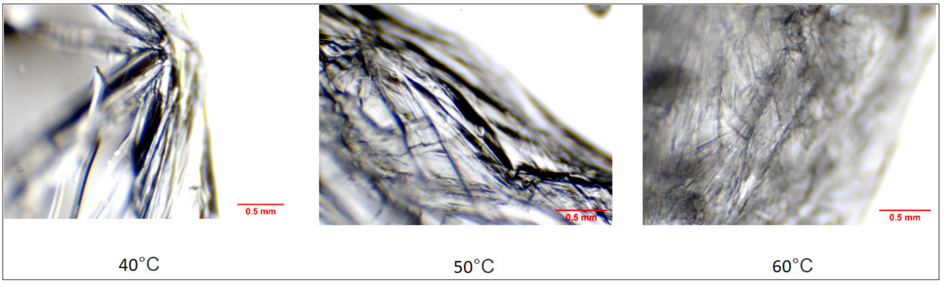

Figure 4. Microscopic photos

The three microscopic photos (Fig. 4) clearly show the effect of the temperature on the nucleation rate- higher temperature leads to more single crystals, and they are tightly packed.

Using different solvents

Purpose: To obtain quantitative data about the relationship between the solvent used and the length of the crystals.

Setup: Solvents (methanol, ethanol, acetic acid) and their mixtures with water are used to dissolve anhydrous $MgSO_4$. The crystals are measured after all of the solvent has evaporated. The crystals were grown in Petri dishes, 10cm in diameter.

Results:

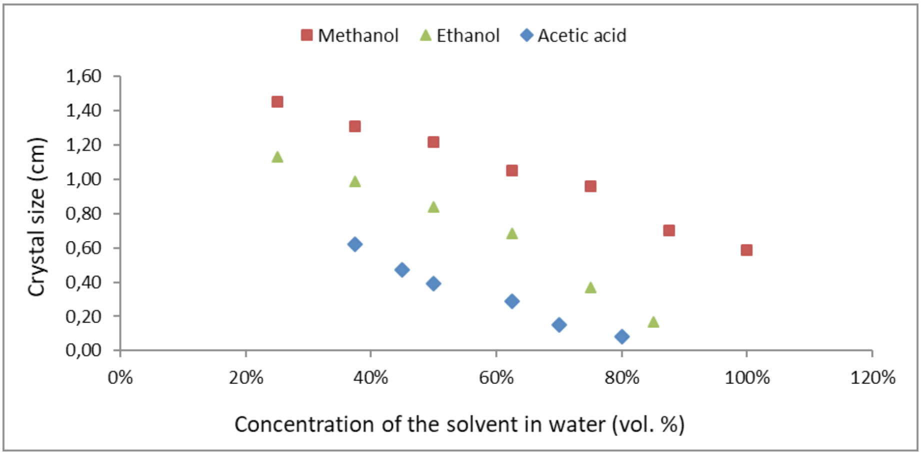

Figure 5. Crystal size using different solvents

The graph (Fig. 5) shows that the longest crystals form from methanol solution and the shortest from acetic acid. All three solvents have vapor pressures higher than that of water and with the addition of water to the solvent, the vapor pressure of the mixture solvent-water decreases. Using this effect and the data from the experiment, we can conclude that the *length of the crystal is inversely proportional to the vapor pressure* of the solvent. However, it is noticeable that although methanol-water mixtures generally have a higher vapor pressure than the rest of the solvents, the length of the crystals is actually bigger compared to the crystals, obtained from the other solvents. A possible explanation for that is the solubility of anhydrous $MgSO_4$ in each solvent. For example, methanol has more than 2 times higher vapor pressure than ethanol, but the solubility of $MgSO_4$ is 30 times higher in pure methanol (Ashford 1994) than in pure ethanol (Weast 1979). That highlights the importance of the *solubility* (Lewis 1997) once again.

Crystals formed from distilled water under room temperature have average length of 0,8cm. Here, although the fact that water has both lower vapor pressure than the solvents mentioned above, and much higher solubility as well, the crystals are shorter. The obtained crystals, however, have a different structure than with the other solvents. They are shorter, wider, and more compact. This is the result of crystallization of large amount of salt in a relatively small volume. From this we can conclude that *mass of solute per volume* is another important parameter.

Collective shape of the crystals

The collective shape of the crystals was different in each sample, although some patterns were observed. The crystals formed tree-like patterns, frost-like patterns, cotton-like patterns, as well as irregular shapes. An example of each type is shown below.

As the pictures show, despite the differences between the patterns, the main similarity between them is that the individual crystals are long and thin. This can be explained using the orthorhombic crystal lattice of $MgSO_4.7H_2O$ (Hennings, Schmidt & Voigt 2013), which allows to form in such way. This can be proved using another salt, which crystallizes in orthorhombic crystal lattice like $ZnSO_4.7H_2O$, where similar patterns were observed1).

Figure 6a. Cotton-like pattern (35% Acetic acid)

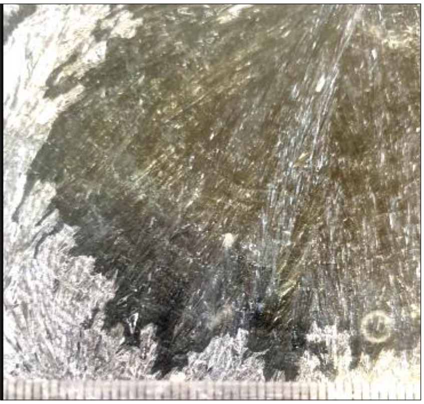

Figure 6b. Frost-like patterns (50% Ethanol)

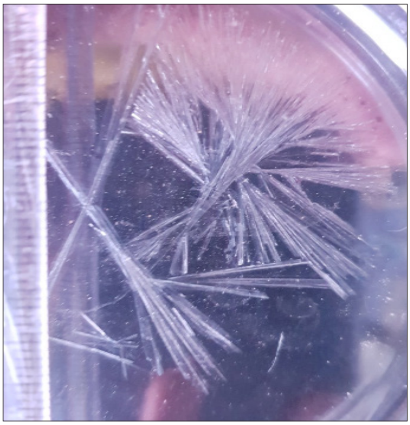

Figure 6c. Tree-like pattern (37,5% Methanol)

The cotton-like pattern (Fig. 6a.) was observed only in the mixtures of acetic acid and water and is characterized with multiple crystal centers with very thin, needle-like crystals growing from each center and these were the object of measurement. The tree-like crystals (Fig. 6b.) are characterized by stem, made of multiple crystals grown together and branches, forming as ray-like crystals from nuclei placed on the main stem. In this configuration, they were the object of measurement. The frost-like pattern (Fig. 6c.) has the most complex structure, which is the result from the stacking of multiple layers of smaller tree-like structures as shown in the microscopic images.

Direction of growing of the crystals

Purpose: To find a relation between the position of the solution towards the walls of a glass vessel and the direction of growing of the crystals.

Setup: Saturated solutions prepared at 50°C are poured onto Petri dishes in one of the three configurations: solution with no contact with the walls of the vessel, solution touching only partially the walls and evenly spread solution.

Results: The images summarize the results obtained from the experiment. The hatched part shows the place of initial formation of crystals and the arrows show the direction of further crystal growth.

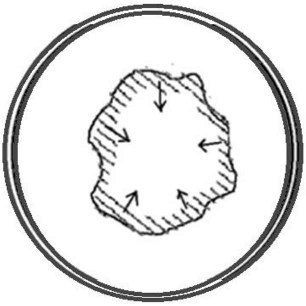

Figure 7a

Figure 7b

Figure 7c

The crystals in the first configuration (Fig. 7a.) firstly form at the periphery of the solution and the crystals grow towards the center. The crystals in the second configuration (Fig. 7b.) grow from the parts of the solution with no contact to the walls of the Petri dish and in the third configuration (Fig. 7c.) crystals form at sporadic spots. The main effect corresponding to the results of the first two configurations is the contact angle of water-glass surfaces (Bourges-Monnier & Shanahan 1995). This effect causes the solution to have more surface area at the periphery compared to the central parts. Since crystals form on the surface because of the evaporation of the solvent, more crystals result being at the periphery. In the third configuration, usually small particles in the air stimulate heterogeneous nucleation (Abyzov & Schmelzer 2014), which creates the sporadic spots. Further in the process, they serve as nuclei for crystal growth.

The average crystal length from all configurations *does not differ* from the result of the corresponding temperature in the previous experiment.

Conclusions

This paper has proved the importance of some parameters, which influence the size and length of $MgSO_4$ crystals. The linearity of the relation between temperature of preparing the solution and the length of the crystals and their inverse proportionality was shown using the qualitative data obtained from the experiment. The effects of the vapor pressure of the solvent and the solubility of $MgSO_4$ in the solvent on the length of the crystals were also shown by comparing data obtained from three different solvents. Three different patterns in the collective crystal shape were recognized and described, but other irregular ones were also observed. All the parameters can be summarized by the following proportion:

$$l \propto \frac{s}{pTc_v},$$

where l – length of the crystals [cm], s – solubility [g/L], p – vapor pressure of the solvent [kPa], T – temperature of formation of the solution [°C], c_v – amount of solute per volume [g/L].

The position of the solution towards the wall of the vessel affects the direction of crystal growth, although it does not have a clear effect on crystal size.

Although the conclusions made in this paper about the factors, which influence the length of the crystals, were made based on experiments using magnesium sulfate, the parameters should have similar effect with different salts and solvents, because the described phenomena are valid with the process crystallization in the general case.

NOTES

1. https://guides.lib.utexas.edu/chemistry/inorganic – Gmelin Handbook for Inorganic and Organometalic chemistry.

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