

Influence of Electric Fields over the Nucleation Ratio of the Lithium – Potassium Sulfate and its Pedagogical Value

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Abstract – This paper presents our research about nucleation and its dependency with external conditions, as well as the internal characteristics of the solution itself. Among the research lines of our group, we have been studying the influence of electric fields over two different but related compounds: *Lithium-Potassium Sulfate* and *Lithium-Ammonium Sulfate*, which both of them show a variation on the *nucleation ratio* when an electric field is applied during the crystal growth. Moreover, in this paper will be explained a laboratory protocol to teach university Science students the nucleation process itself and how it depends on external applied conditions, e.g. electric fields.

Index Terms – Crystallization techniques, electric fields, laboratory protocol, learning material, nucleation.

I. INTRODUCTION

Nucleation is the phenomenon which precedes crystal growing. During this phase, the constituent atoms or molecules experiment a process of *self-assembly* in order to form a *cluster* or *nucleus*. When this one reaches a proper size, the crystallization process itself begins. Nevertheless, this phenomenon is not only related with the crystal growing but there are so many examples in nature, as for instance the formation of the water drops in the clouds or the self-assembly of the viral capsids.

And it has been well-known from decades ago that there are two different processes for the nucleation: the *heterogeneous* and the *homogeneous nucleation*. The first one occurs over *nucleation sites* or surfaces in the system as for instance, impurities on the environment. On the contrary, the homogeneous nucleation does not need any surface. However, whereas in both cases the cluster must reach the same size to start the crystallization, the energy requirement for the heterogeneous nucleation is fewer than in the case of the homogeneous one.

In general, this phenomenon depends on the properties of the *solution* from which the crystals are obtained but it can also be altered by means of external fields, e.g. an *applied electric field*. In particular, our group has been researching into the effects of this kind of fields over the nucleation ratio for *Lithium-Potassium Sulfate (LKS)* and *Lithium-Ammonium Sulfate (LAS)*.

II. JUSTIFICATIONS AND OBJECTIVES

Teaching of the nucleation process is fundamental for the education of future undergraduates all over world, as this stands as an important part during the process of crystal growing which can be significantly affected by the *nucleation ratio*. Therefore, this process has been included into the formation programs at university level for many years, both for compulsory courses and for elective ones. In particular, at the *Section of Physics (Faculty of Science) of La Laguna University* it can be studied during courses as *Physics of Solid State*, *Physics of the Atmosphere and Obtaining and Characterization Techniques of Materials*.

Therefore, in order to reach a better understanding of this phenomenon by the students, not only a theoretical explanation but also an experimental one must be given to them. The purpose of this paper is to explain a *laboratory protocol* to study the nucleation phenomenon and how it can be altered by means of an application of different conditions; in particular an applied electric field.

III. THEORETICAL AND EXPERIMENTAL BACKGROUND

Nucleation process is going to be studied supposing a *supersaturated aqueous solution* into which the *solid phase or cluster* is growing in thermal equilibrium with the solution. And for the purpose, the variation on the *Free Gibbs Energy* is analysed. In general:

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta G_v \quad (1)$$

Where r is the *radius of the cluster*, σ the *interfacial tension* and ΔG_v is the variation on the Free Gibbs energy between the aqueous and solid phases per unit of volume.

The first term is associated with the cluster's surface and it represents *the work to create a new interfacial surface*. This one is always positive, so it increases the Free Gibbs Energy variation. The second term, related with the volume of the cluster, represents the work to

move an atom or molecule from the liquid phase to the solid one and it decreases the Free Energy variation. This last one can be written as follows:

$$\Delta G_v = \frac{\Delta \mu}{V_m} = \frac{\mu_a - \mu_s}{V_m} \quad (2)$$

With V_m is the volume of the cluster and $\Delta \mu$ is the variation on the *chemical potencial* between the aqueous and solid phases. And again, this last term can be rewritten as:

$$\Delta \mu = k_B T \ln \left(\frac{C}{C_s} \right) = k_B T \ln S \quad (3)$$

Where k_B the *Boltzmann constant*, T the temperature of the solution and S the *supersaturation ratio*.¹

And finally, if (1) is minimized by respect to the radius and by means of (2) and (3) and expression for the *critical radius* (r^*) can be obtained:

$$r^* = \frac{2\sigma V_m}{k_B T \ln S} \quad (4)$$

Which corresponds with a *Critical Free Gibbs Energy variation* (ΔG^*) of:

$$\Delta G^* = \frac{16\pi\sigma^3 V_m^2}{3(\Delta \mu)^2} \quad (5)$$

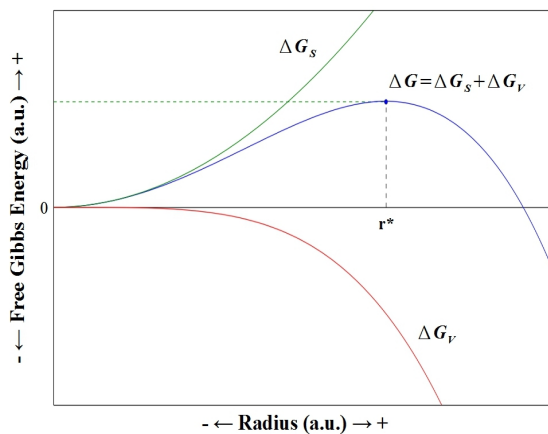


Figure 1. Variation of the Free Gibbs Energy during the cluster growing and the contribution of the surface and volume terms.

And that critical radius represents the minimal size the cluster must reach in order to start the crystallization process. Until the cluster gets that radius, the growing of this one is an energy-unefficient process which occurs due

1 C represents the actual concentration of the solution and C_s the saturation concentration.

to fluctuations into the system. In *Figure 1*, the contribution of the surface and volume terms, as long as the global effect of these two ones over the Free Gibbs Energy variation is given.

Now, we can consider the effect of an external field over this energy variation by the addition of a new term into (1) [1]:

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta G_v + \Delta G(E) \quad (6)$$

With $\Delta G(E)$ the variation on the Free Gibbs Energy due to the influence of the electric field. And this term has the next following expression [1]:

$$\Delta G(E) = -\frac{9g\omega\epsilon_0 k_a (k_a - k_c) E^2}{2(k_c + 2k_a)(2 + k_a)^2} \quad (7)$$

Where g is the number of molecules or atoms in the cluster, ω the volume per molecule or atom, ϵ_0 the vacuum permittivity, k_a and k_c the dielectric constants for the aqueous solution and the cluster.

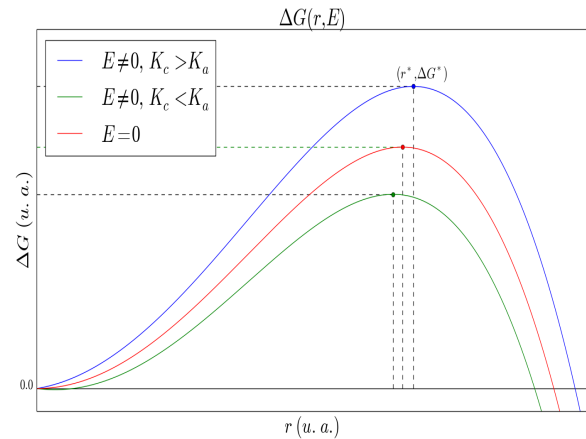


Figure 2. The effect of the electric field over the nucleation process consist of a variation in the critical radius and Free Gibbs Energy.

According to (7), the electric field produces a variation in the Free Gibbs Energy. This variation can be positive or negative depending on the relation between k_a and k_c . If k_a is bigger than k_c when an electric field is applied, $\Delta G(E)$ will be negative and then, the critical radius and Free Gibbs Energy will be reduced. When this parameters have a contrary relation, the influence will be an increasement of the critical radius (*Figure 2*).

Within this framework, our research group has been investigating the influence of electric fields over the crystal growth of *LKS* (*Figure 3*) and *LAS* [2], growing these materials under applied fields of 2000, 4000 and 8000 V/m; adding a growth without any electric field as a control sample.

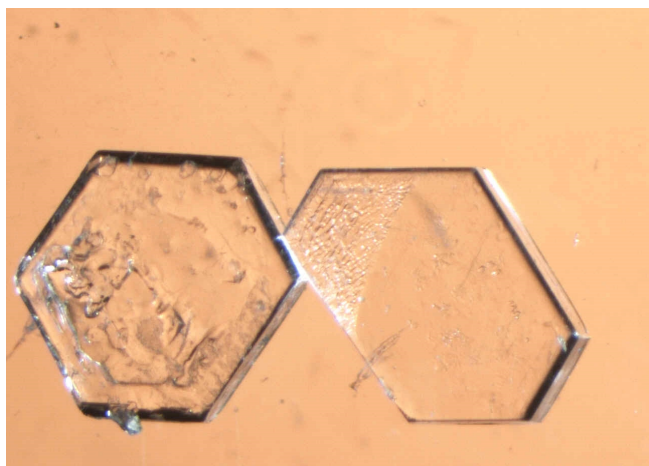


Figure 3. Typical hexagonal habit of the Lithium – Potassium Sulfate. These crystals were obtained by the slow evaporation method at 40 °C with an applied electric field of 4000 V/m.

For these compounds, a significant variation in the nucleation ratio has been found when the growth is performed under 4000 V/m and at 40 °C. Under these conditions, a reduction in the number of crystals can be observed when it is compared with the sample obtained without any electric field. Nevertheless, these crystals are bigger, so it can be supposed an increment in the critical radius, producing fewer nuclei which reaches that size and then, any of them have more molecules to grow (Figure 4).



Figure 4. Comparing between the growth obtained without any electric field (left) and an applied one of 4000 V/m (right). It can be notice a variation on the number and size of the crystal which were obtained.

IV. EXPERIMENTAL METHOD

For this experience, and with a pedagogical aim, it will be only used the LKS to study the influence of electric fields over the nucleation process. This is due to the fact that whereas the LKS grows in only three days when the experiment is performed at 40 °C, it takes to the LAS a week to grow. So, using the LKS the student can appreciate the effect of the electric field during a short period of time.

A. Crystal Growing Device and Experimental Set-up

To perform the experience, the student will have two principal device sets, first one to synthesize the LKS and another one to apply electric fields over the sample in order to perform the crystal growth under these new conditions.

For the synthesis it will be used two *petri dishes* as crystallizers (Figure 5), a *copper adhesive tape* which is used to cover the plates, required *reagents* for the synthesis reaction, *double distilled water*, *magnet stirrer*, *test tubes* and a *precision scale*.

Once the solution is obtained, a *DC generator* will be connected to the plates by means of the copper to produce a *vertical electric field*, working this device as a *capacitor*.

The purpose for this laboratory practice is to study the influence of an electric field over the crystal growth. For this experience, 30 ml of LKS in aqueous solution at 1.5 M will be done. Finally, two growths will be synthesized from this solution: one without any applied electric field (*control sample*), and another one under a field of 4000 V/m.



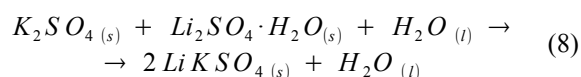
Figure 5. Top of the crystallizer made with a petri dish covered by adhesive copper. In this picture the holes are only placed over the half of the plate. The dimensions of the dish are 6 cm in diameter and 1.5 cm in deep.

B. Laboratory Protocol

As we introduce in section A, the experiment is split in two parts: the first one is the synthesis of the LKS solution, and the growth itself.

For the synthesis of high quality crystals, and following the experience obtained by our research group after many years synthesizing these materials, it will be applied the *slow evaporation method* at a constant temperature of 40 °C by means of an oven.

First, the student has to verify the calculations given in Table 1 to earn the amount of each reagent needed to synthesize 30 ml of LKS solution at 1.5 M, according to the following reaction:



Given that the reaction keeps a relation 1:2 molar between reagents and LKS respectively, so the student can deduce how many grams of each reagent are needed. Once the calculations have been verified the

solution for each reagent will done isolated, keeping it in stirring for an hour and subsequently, putting them together and let it blend for another hour.

Reagent	Solute (g)	Solvent (ml)
$Li_2SO_4 \cdot H_2O$	2.908	9.430
K_2SO_4	3.003	19.077

Table 1. Calculations for the LKS synthesis. The grams are calculated taking account that the reagents were used at a 99% of purity. The ml are obtained according to the solubilities.

The cause of the isolation is due to the great different solubilities of each compound. According to the experience of our research group, the best temperatures to obtain the solutions for each one are at *room temperature* for the $Li_2SO_4 \cdot H_2O$ (over 20°C) and 40 °C for the K_2SO_4 . At these temperatures, the solubilities are 0.308 gr/ml and 0.157 gr/ml, respectively.

And, as can be observed in Table 1, each reagent needs different amount of water, so it will be used 20 ml to prepare the K_2SO_4 and 10 ml for the $Li_2SO_4 \cdot H_2O$ solution.

Meanwhile the solutions are being agitated the student has to perforate the petri dishes, and cover just one of them with *copper adhesive tape*. The location of these perforations will done just in a half of the plate. The reason is, and according to previous experiences, if the whole petri dish is perforated, *Copper Sulfate* which appears around the holes interrupting the conductivity and then, avoiding the production of the electric field. Moreover, doing the same perforations in both plates ensure an equal evaporation rate in both growths.

Finally, the synthesis procedure ends by filtering the solution, previous to put them into the crystallizators.

Then, to achieve the crystal growth and to warrant a constant electric field, the level of solution used in both petri dishes must be high enough to fill them up, allowing to consider a *constant electric permittivity* all along the path of the electric field.

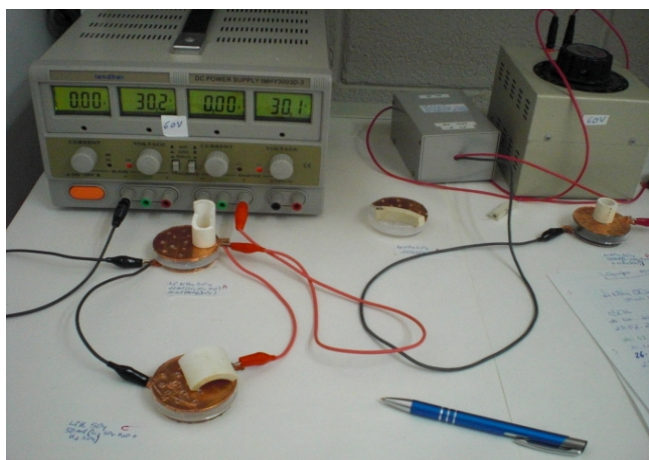


Figure 6. The final setting for crystal growth; two DC generators were connected to the plates with LKS solution.

Finally, the connections must be done with the positive pole at the top of the plate and the negative one at the bottom. After that, the dishes must be placed in a *free vibration environment* during three days (Figure 6). Then, the number of crystals in each dish must be counted to determine the difference in the *nucleation ratio* according to the growth conditions.

V. FUTURE GUIDELINES

The next step to follow with this investigation is to research about the synthesis of LKS by means of the slow evaporation method at 40 °C with crystal seeds and mixing. To perform this kind of crystal growth our research group has designed a new device which ensure that conditions (Figure 7). This device will be also used in the laboratory practices given by our group in the different courses imparted by our group.

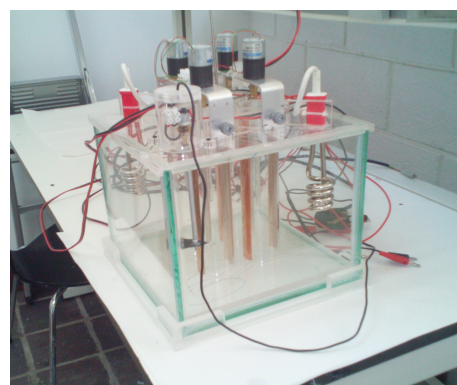


Figure 7. Device built to perform the crystal growth constant temperature, using seeds and applying mixing into the solution to avoid the formation of subsaturated areas.

VI. CONCLUSIONS

The understanding of the nucleation process is fundamental in the curriculum of a Science student because this step has an enormous effect over the crystal growth itself and it allows to comprehend this phenomenon.

Therefore, by means of this experience, the student is able to understand not only the nucleation process but also the influence of an external field, in particular an electric one over a crystal growth.

REFERENCES

- [1] K. V. SABAN (2003). *Nucleation kinetics in crystallization under electric and magnetic fields. Chapter 4: Thermodynamics and kinetics of crystal nucleation in electric and magnetic fields*. Tesis. Kottayam: Mahatma Gandhi University.
- [2] D. RAMOS HERNÁNDEZ (2015). *Aplicación de campos eléctricos sobre el crecimiento cristalino del $LiKSO_4$ y del $LiNH_4SO_4$: Influencia sobre sus propiedades polimórficas*. Degree final project. Spain: Faculty of Science, Section of Physics, La Laguna University.