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Sono-crystallization of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

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Abstract

Power ultrasound are known to enhance crystals nucleation, and nucleation times can be reduced by one up to three orders of magnitude for several organic or inorganic crystals. The precise mechanism of this phenomenon is yet unclear, but various theoretical explanations involve the action of inertial cavitation bubbles: cooling effect, pressure effect, segregation effect and evaporation effect. All these effects sound reasonable and may in fact act in a complementary fashion. The pressure effect is mediated by the high pressures appearing near the bubble as the latter collapses. The increase in pressure shifts the thermodynamical equilibrium. Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) has the interesting property that its solubility is not sensitive to pressure. We therefore carried out experiments of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystallization by cooling in a 0.5 L crystallizer, both under silent conditions and by 20 W/cm² insonification with a horn transducer. The induction time is found almost independent of supersaturation under ultrasound, and much lower than the one obtained in silent conditions for low supersaturation (0.021 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ / g solution). These experimental results question the generality of the pressure effect.

Keywords : Ultrasound ; Mechanisms ; Pressure effect ; Crystallization ; Induction time

1. Introduction

Crystallization is a process used in many industrial domains including chemical, pharmaceutical and petrochemical industries, and usually considered in terms of nucleation and crystal growth [1]. Works on the influence of ultrasound in crystallization processes have been published for several years. The positive influence of ultrasound (US) on crystallization processes is shown by the drastic reduction of the induction time, supersaturation conditions and metastable zone width [1]. The precise mechanism of this phenomenon is yet unclear, but various theoretical explanations involve the action of inertial cavitation bubbles on supersaturation or/and molecular aggregation.

The expression of supersaturation as function of temperature and pressure is given by :

$$S = \frac{C}{C^*(T, P_0)} \exp\left[\left(\bar{v}_L - v_s\right) \frac{(P - P_0)}{(k_B T)}\right] \quad (1)$$

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where \bar{V}_j is the molar volume of solute and v_s the molar volume of crystal.

Four explanations could be proposed:

- cooling hypothesis: cooling during the bubble expansion induces an increase of local supersaturation leading to nucleation of crystals at the vicinity of bubbles in the case of product with a solubility increasing with temperature.
- pressure hypothesis: high pressures modify the local supersaturation and may promote nucleation in the case of product with a solubility decreasing with pressure [2].
- evaporation hypothesis: solvent evaporation into the bubble implies an increase of solute concentration leading to an increase of supersaturation (yet unexplored).
- segregation effect: it has been recently proposed, and quantified theoretically [3], that the large pressure gradients appearing near the bubble at the end of the collapse could segregate the solute from the solvent, for a very short time at the end of the collapse.

All these effects sound reasonable and may probably in fact act in a complementary fashion. The pressure effect has been used and tentatively quantified by virone et al. combined overpressure calculation near the bubbles and classical nucleation theory to deduce the reduction of induction time of ammonium sulphate. However, the measured and calculated induction time did not match. This hypothesis is valid when the solid phase is denser than the solute form. However, strong reduction of induction times have been observed for crystals that are less dense in the solid phase than in solute form (glycine [4], potassium sulphate [1]). This demonstrates that the pressure effect alone cannot explain all experimental results. For both the cooling effect and the pressure effect, the key parameter is the solubility curve of the crystal as a function of temperature and pressure. Solubility generally increases with temperature, and may exhibit various behaviors as a function of pressure.

Zinc sulphate heptahydrate is an interesting solid, which its solubility in water is not sensitive to pressure $\Delta V = v_L - v_s = 0$ [5].

The solubility of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in water increases as a function of temperature [6]. We therefore carried out experiments of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystallization by cooling, under silent conditions and in presence of ultrasound by a horn transducer, with an intensity around 20 W/cm².

2. Experiments

Aqueous solutions are prepared from zinc sulphate heptahydrate crystals (Riedel- de Hain purity min 99%) and ultra pure water (18,2 M Ω .cm⁻¹). The experimental apparatus used for the determination of induction time consists of a thermostated vessel (400 ml) stirred with a magnetic rod at a constant rotation speed of about 500 rpm (Figure 1).

Ultrasound is applied at the top of the vessel by a stainless ultrasound transducer. Two ultrasonic power levels have been used: 16 and 30 W measured in water by the calorimetry method. The solution temperature is measured with an instrumental resolution of 0.01 °C. We consider that the appearance of crystals is detected when there is a sudden increase of temperature because the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ presents a high crystallization enthalpy estimated around -16.624 kJ/mol [7].

Before each experiment, in order to dissolve all crystals, suspensions are heated to a temperature higher by 8 °C than the saturation temperature during 1 hour. The initial saturation temperature (T_{sat}) is ranged from 28 to 32 °C. The solution is rapidly cooled to 25 °C. Ultrasound is applied at the end of the cooling phase (≈ 12 min). The induction time is measured as soon as the temperature 25 °C is reached or when ultrasound is applied at the end of cooling.

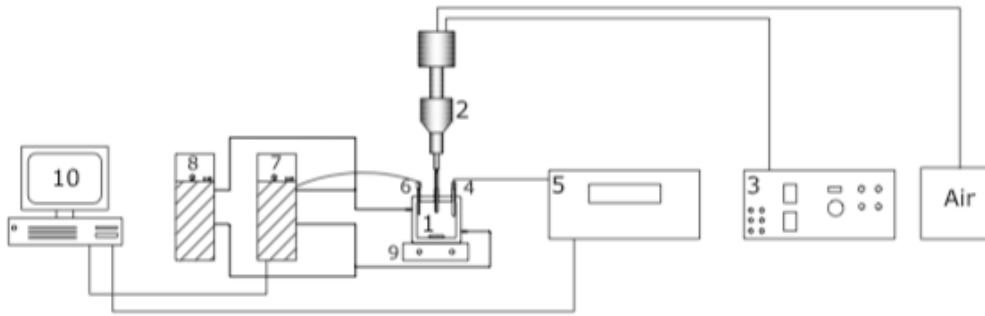


Fig.1 Experimental set-up. 1: Thermostated vessel 2: Sonotrode 3: Generator of ultrasound 4: Probe of temperature 5 and 6: Two baths 7: Magnetic agitator 8: Computer.

3. Results and discussion

3.1. Induction time

Fig 2 and Fig 3 present the temperature profile applied (heating, dissolution, cooling, and plateau at crystallization temperature). The increase of temperature observed on the plateau corresponds to the appearance of solid.

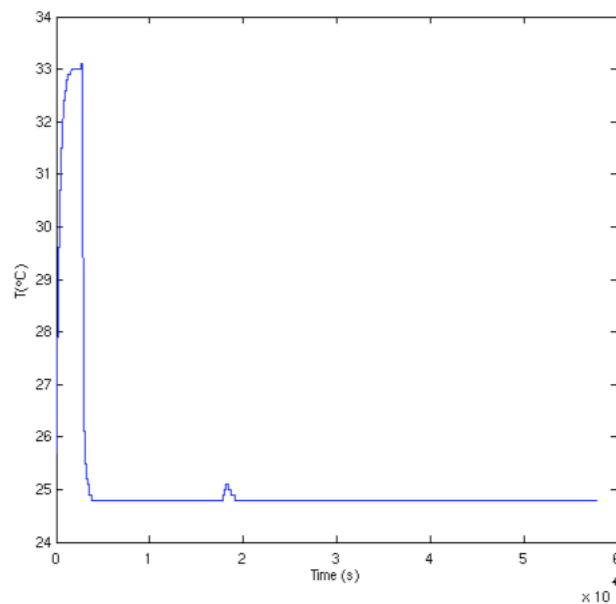


Fig.2 Experiment without ultrasound, $\Delta C = 0,021$ (g of hydrated salt / g of solution), cooling time = 12 min, temperature of dissolution = 36°C , induction time = 229 min.

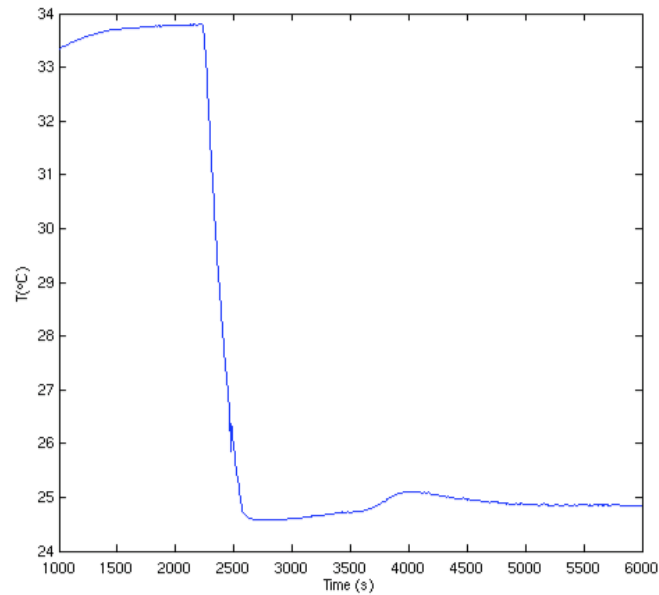


Fig.3 Experiment with ultrasound, $\Delta C = 0,021$ (g of hydrated salt / g of solution), cooling time = 12 min, temperature of dissolution = 36 °C, dissipated power = 16W, induction time = 16 min.

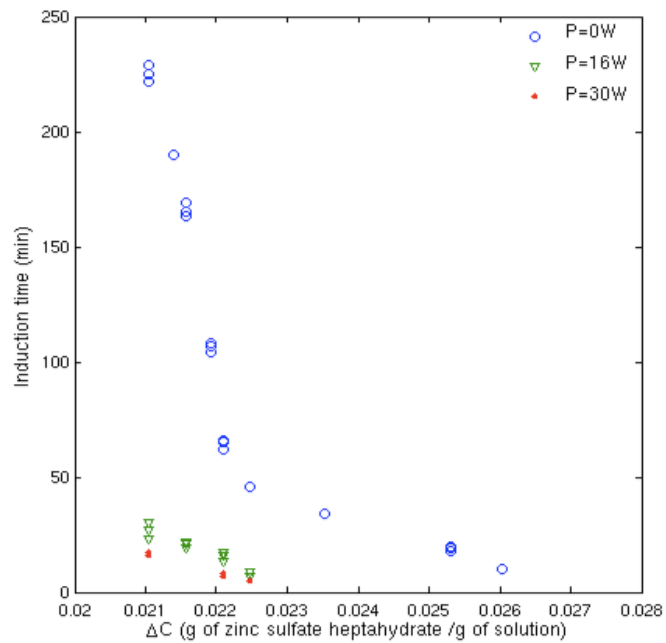


Fig.4 Induction time of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as a function of supersaturation in silent conditions (circles), insonification with $P=16\text{W}$ (triangles) and insonification with $P=30\text{W}$ (stars).

The variation of induction time versus absolute supersaturation is presented in Figure 4. The absolute supersaturation is calculated as the difference between the initial concentration and the saturation concentration at crystallization temperature around 25 °C for the hydrate form.

Figure 4 shows that the induction time is found to be almost independent of supersaturation under ultrasound, and much lower than the one obtained in silent conditions for low supersaturation (< 0.022 (g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ / g of solution)). This effect is less significant at high supersaturation when nucleation is very fast anyway. The behaviour without ultrasound agrees with classical results on induction time.

3.2. Structural characterization

The figure 5 presents the X-ray powder diffraction spectrum of one powder crystallized without ultrasound and two powders crystallized with two different ultrasound powers (16 and 30 W). The same orthorhombic structure is found. Ultrasound did not modify the network crystalline $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Indeed, some peaks appear at the same position. So, there is no atoms insertion and no creation of gaps.

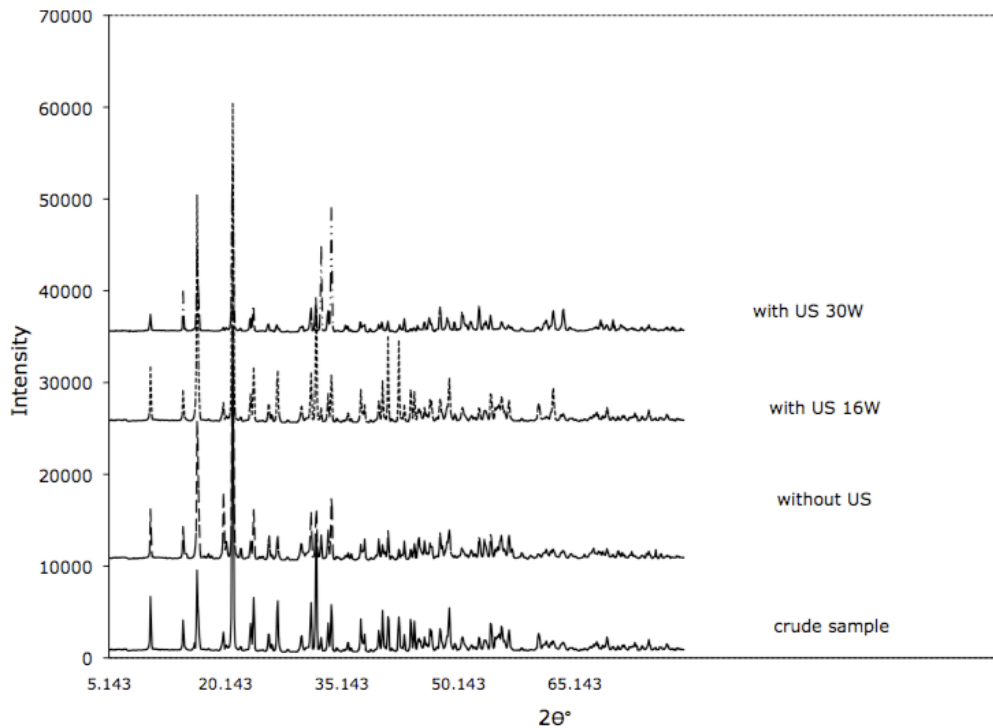


Fig.5 X-ray powder diffraction spectrum of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

4. Conclusion

An increase of pressure does not change supersaturation of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ but ultrasound permits to strongly decrease of the induction time of this salt. These experimental results on induction time and those obtained for potassium sulphate question the pressure effect hypothesis on nucleation.

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