

Metastable Limits of Salts: Measurements and Consequences

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The applicability of ultrasonics for the determination of the limits of the metastable zone of inorganic salts was examined. It was found that the ultrasonic technique can be successfully employed to measure the saturation and nucleation points of different solutions with adequate accuracy. The characterization of the metastable zone of KCl and NaCl solutions as a function of the ultrasonic velocity and temperature was established to be a feasible method for in-situ measurement of the metastability of supersaturated solutions in crystallization processes even in the presence of impurities. The continuous measurement of the supersaturation by means of ultrasonics was established to enable the control and automation of crystallization processes. By using the ultrasonic measuring device for process control, optimum process conditions could be obtained, which results in an improvement in product quality, i.e. purity and crystal shape, as well as also often in an optimization of space-time-yields.

1. INTRODUCTION

Supersaturation is the prerequisite for nucleation and crystal growth, which are decisive not only for crystal formation, but also for the properties of a crystalline product. Every solution tolerates a maximum amount of supersaturation before it becomes unstable and spontaneous nucleation occurs. The zone between the saturation curve and this unstable limit is called metastable zone. In this zone all crystallization processes take place. However, in contrast to the saturation curve, the supersaturation limit is thermodynamically not defined. It depends on parameters such as temperature level, cooling rate, use of agitation, presence of impurities etc.

When crystallization occurs at high supersaturations usually small crystals or crystals with many liquid inclusions are obtained. However, crystallization taking place at low supersaturations leads to a rather slow growth and is therefore not of interest for economical and operational reasons. The optimum supersaturation point for crystallization generally lies in the middle of the metastable zone. Hence, it follows that if the aim is to obtain a certain product having a specific crystal size distribution, shape and purity, instead of a random product, it is necessary to control the local and mean supersaturation [1].

In this contribution a novel technique by means of ultrasonic velocity measurement [2, 3] is used to determine the width of the metastable zone of NaCl as well as KCl in dependence of temperature and impurities.

2. ULTRASONIC MEASURING PRINCIPLE

The principle of the ultrasonic velocity measurement is based on time-measuring. At periodic intervals, a piezo-transmitter emits an ultrasonic signal which is detected by the receiver and is amplified. The running time of the sound pulse through the constant distance, s , between transmitter and receiver as well as the temperature of the medium are continuously measured. In Figure 1 the measuring principle is shown.

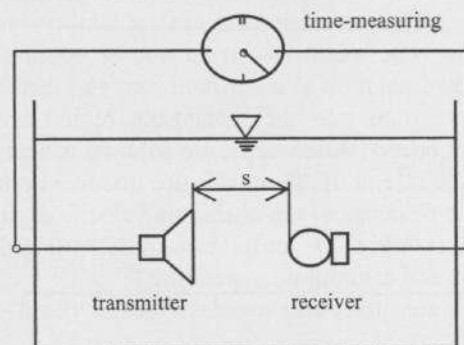


Figure 1. Ultrasonic measuring principle [4]

The ultrasonic velocity in liquids depends on the density, ρ , and the adiabatic compressibility, β_{ad} , of the medium. Both, density and adiabatic compressibility, are temperature, concentration and pressure dependent physical properties.

The dependence of the ultrasonic velocity on the adiabatic compressibility and the density is presented by the following equation:

$$v = 1/\sqrt{\beta_{ad}\rho} \quad (1)$$

In more component systems, the total sonic velocity depends on the sonic velocity of the pure materials, temperature, pressure, concentration and the interaction between the present components in the system [4, 5, 6]. Since the spreading rate of ultrasonic waves strongly depends on temperature, the ultrasonic velocity measurement over the concentration range of 'a specific solution' does not result in a single characteristic curve but in a field of characteristic curves (see Fig. 3, which is explained subsequently).

3. EXPERIMENTAL METHOD AND APPARATUS

The different experimental solutions are prepared by adding analytical grade potassium chloride or sodium chloride to deionized water. To achieve the varying impurity concentrations of Pb^{2+} -ions, analytical grade $PbCl_2$ is added. The ultrasonic velocity and temperature of the prepared solutions are measured using a submerged LiquiSonic 30 sensor developed by SensoTech GmbH, Magdeburg, Germany.

The crystallizer consists of a one liter jacketed glass vessel, which is brought to the desired temperature using a water-operated thermostat. Each solution is initially heated about 5°C above the saturation temperature. At that point the solution is stirred vigorously for two hours to ensure the dissolution of all fines. The measurement of solubility and metastable zone width is carried out by cooling a nonsaturated solution at a constant rate and thereby moving its state into the metastable region until nucleation occurs. Afterwards, the solution is heated at the same rate until all crystals are dissolved once again. The response of the ultrasonic velocity during this cycle (see Fig. 2) can be used to determine the nucleation and saturation temperature.

Apparatus and procedure are described in detail by Omar [7].

4. EXPERIMENTAL RESULTS

4.1 Determination of the metastable zone of KCl

The point of nucleation as well as the point of saturation can be determined by measuring the change in the spread velocity of ultrasonic waves through the liquid media. This enables the determination of the metastable zone width of organic as well as inorganic crystallizing materials.

In Figure 2 the measured changes in the ultrasonic velocity of the solution with changing temperature during a cooling or heating cycle, respectively, are presented. The course of the ultrasonic velocity during this cycle can be used to determine the saturation and nucleation point and with that the metastable zone width at constant concentration.

The indicated saturation and nucleation points in Figure 2 have been optically determined. Systematic deviations of approximately 0.2°C between the optically determined and the measured nucleation and saturation points are due to a lack in sensitivity of this laboratory measuring device. However, using an improved measuring device having an adjusted frequency range will also enable the detection of only slight changes in density. Therefore, the ultrasonic measuring technique represents a suitable device for the control of crystallization processes, even for substances with small metastable zone widths.

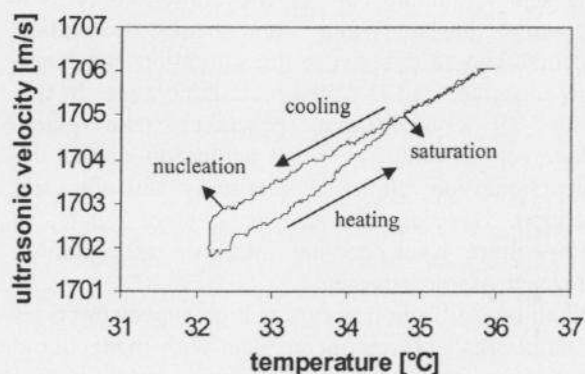


Figure 2. Nucleation and saturation point of a potassium chloride solution at a concentration of 27,9 wt%

In the case of potassium chloride, the ultrasonic velocity decreases linearly with decreasing temperature. Cooling the solution is moving the solution from the nonsaturated state through the

saturation point into the supersaturated state (metastable zone). With further cooling of the solution, nucleation is taking place. At the beginning of nucleation, a sudden, distinct decrease of the ultrasonic velocity is recorded. The starting point of this decrease of the ultrasonic velocity can be used to determine the supersaturation limit of the metastable zone. Heating the suspension directly after nucleation will result in a dissolution of the solid particles in the solution. During heating of the suspension, the ultrasonic velocity increases linearly with increasing temperature. At the point of subsequent complete disappearance of the solid phase in the solution, the dissolution curve intersects with the cooling curve at the saturation point. This point of intersection can be used to determine the saturation point of the metastable zone.

To measure the degree of supersaturation of a solution during crystal growth in a seeded batch crystallizer, it is necessary to characterize the metastable region as a function of the measured variables (ultrasonic velocity and temperature). In crystallization processes the concentration of the solution changes during crystal growth. Since the limits of the metastable zone are a function of the concentration, for optimum execution of crystallization processes it is required to characterize the metastable region in the concentration range at which the crystallizer is operated. The linear temperature dependence of the ultrasonic velocity in the course of constant cooling of the solution within the metastable region can be used to characterize the metastable zone as a function of the ultrasonic velocity and temperature at different concentrations.

The measurement of the metastable zone width for primary nucleation of KCl over a temperature range of 30°C is depicted in Figure 3. Such measurements can be used to determine the supersaturation of a solution or the point in the metastable zone at which the crystallizer is currently operated.

A comparison between nucleation of a pure solution and in the presence of KCl-crystals at a saturation temperature of 50°C is shown in Figure 4. In the latter case, 0.1g seed crystals with a size cut of 400-450 μm have been added to the saturated solution. As can be seen in Figure 4, in the presence of crystals, nucleation sets in after a shorter induction time than in the case of the pure solution.

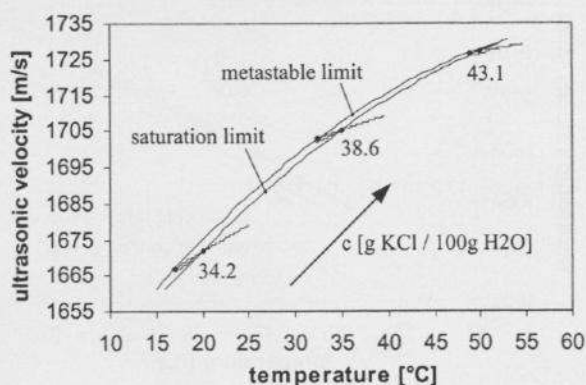


Figure 3. Metastable zone width of KCl over a concentration range between 34.2 and 43.1 g/100g H_2O at a constant cooling rate of 4K/h and moderate stirring

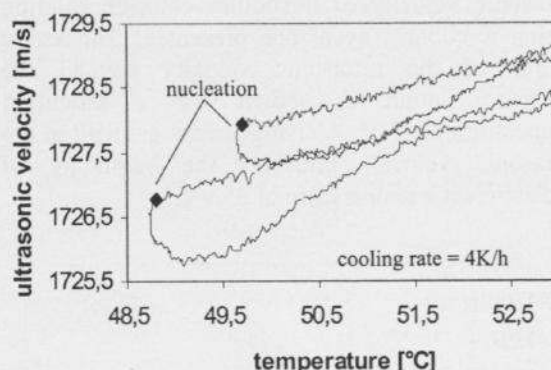


Figure 4. Comparison between nucleation of a pure solution and in the presence of crystals

4.1.1 Influence of lead ions on the metastable zone width of KCl

The metastability of a supersaturated solution or the operating point of the crystallizer in the metastable zone can be affected drastically even by small amounts of additives.

The effect of the presence of Pb^{2+} -ions on the crystallization behavior of KCl is presented in Figure 5. As can be seen in Figure 5, the maximum supercooling increases with increasing lead concentration. The measured increase in the saturation temperature can be attributed to the decrease of the dissolution rate of KCl in the presence of lead ions. It has been determined experimentally that the added amounts of lead ions have a negligible effect on the saturation temperature.

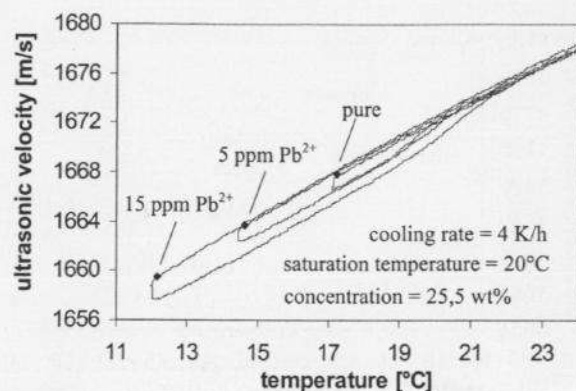


Figure 5. Influence of lead ions on the metastable zone width of KCl

4.2 Determination of the metastable zone of NaCl

In Figure 6 the measured changes in the ultrasonic velocity of a sodium chloride solution during a cooling cycle are presented. The entire course of the ultrasonic velocity beyond the nucleation point is shown for a saturation temperature of 35°C. A change in the gradient of the ultrasonic velocity indicates the beginning of nucleation at a temperature of 26,9°C.

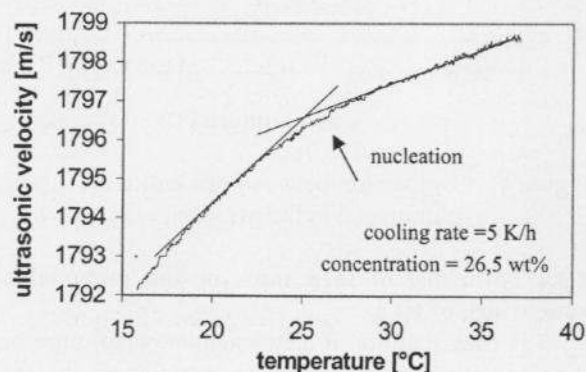


Figure 6. Metastability of NaCl

5. COMPARISON BETWEEN LITERATURE AND EXPERIMENTAL DATA

Although in technical literature numerous statements about metastable zone widths for a multitude of substances exist, these data are often not suitable for practical application. Literature data lack in most cases details concerning the experimental parameters, i.e. experimental apparatus, temperature level, cooling rate and the kind of

agitation. Due to this missing information, considerable deviations between the own experimental and literature data cannot in detail be explained. In Table 1 a comparison between literature data and our own experimental data is shown. Although in both cases the experiments have been carried out using moderate agitation and a slow cooling rate, considerable deviations in the maximum super-cooling for NaCl occur. The strong influence of temperature and experimental conditions is made clear in Table 2. The width of the metastable zone changes distinctly with temperature level and cooling rate. Since the metastable limit is thermodynamically not defined and therefore even under constant process conditions no exactly reproducible results can be achieved, the relevance of literature data for practical application can in most cases only be seen as a 'first clue'.

Table 1
Metastable zone widths [K]

	Literature data [8]	Own experimental data
KCl	1,1 (at 25°C)	1,2 (at 20°C)
NaCl	1,0 (at 25°C)	8,1 (at 35°C)

Table 2
Metastable zone widths [K]

	Literature data [9]
KCl	1,62 (at 29,8°C, 2°C/h cooling rate)
	1,86 (at 29,8°C, 5°C/h cooling rate)
	1,02 (at 59,8°C, 2°C/h cooling rate)
	1,18 (at 59,8°C, 5°C/h cooling rate)

6. DISCUSSION

In the field of the control and automation of industrial batch crystallization processes it is usually required to have updated information about the limits of the metastable region, because these limits change with the operating conditions and the concentration of additives. The presence of additives can change drastically both, the nucleation as well as the saturation limits of the metastable zone (see e.g. [11]).

If the concentration and the type of additives in a feed solution change frequently, it is required for optimum process conditions to get updated

information about the saturation and the nucleation limits before setting a control strategy of a process. Such essential information need fast and practical methods to determine the limits of the metastable zone.

The ultrasonic technique can supply fast information on the saturation and nucleation limits independent of the solution composition or color or transparency with reliable precision.

7. CONCLUSIONS

The aim of this contribution was to test the feasibility of the ultrasonic technique for the measurement of the limits of the metastable zone for inorganic salts. It was found that the ultrasonic technique is a feasible and fast method to determine the saturation and nucleation limits of a solution with adequate accuracy. Since the ultrasonic technique can be used to measure on-line and in-line the supersaturation of solutions as well as the effect of additives on the metastability, this technique offers a very convenient method to develop and control the operations of crystallization processes. By sole control of temperature, effects on the width of the metastable zone as for instance caused by changing additive concentration and temperature level cannot be considered. A continuous measurement of the supersaturation by means of ultrasonics enables the control and automation of crystallization processes and therefore optimum process conditions can be achieved. Consequences of the process optimization by means of ultrasonics are improvements in product quality, i.e. purity and crystal habit, as well as often also in product quantity, due to the operation always in the optimum concentration point, in the case of continuous operations in the middle of the metastable zone [10].

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SYMBOLS

v	[m/s]	ultrasonic velocity
β_{ad}	[1/Pa]	adiabatic compressibility
ρ	[kg/m ³]	density

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