Cryst. Res. Technol.	26	1991	1	35–42

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The Detection of Salting-out. A Comparative Study

We present a new device for the measurement of the metastable zone width and related parameters. The salting-out is detected by using simultaneously seven different methods: a) visual detection, b) intensity of the transmitted laser beam, c) noise associated to (b), d) intensity of the reflected laser beam, e) noise associated to (d), f) conductivity, and g) pH. Full computerization permits an easy and quick take of data on the evolution of the nucleation and crystal growth processes. The use of this apparatus shows that the waiting time for the growth component of the induction time is minimized for the method using the noise associated to the reflected light as the recorded parameter. This comparative study shows that the maximum undercooling and maximum allowable supersaturation values obtained by the different tested methods present significant differences between each other. Meanwhile, we propose that the tabulated values of such parameters should specify the experimental way followed for the obtainment of reliable data.

1. Introduction

The process of nucleation of a supersaturated solution is characterized by a waiting time or induction time, τ, which is equal to the summation of three variables (NÝVLT): t_s, which is the waiting time required to produce a stationary distribution of nuclei; t_n, which is the time required for the nuclei to pass the critical size, and t_g, which is the waiting time required for the nuclei to reach the detectable size by the method being used. The first two quantities are dependent upon the characteristics of the solute-solvent system whereas the third one depends on the experimental technique used for the detection of the first formed nuclei of the precipitate. Literature on industrial crystallization lists different measuring techniques for these variables (JANSE, DE JONG; DE JONG), and their use is a source of problems in extrapolation and of disagreement in experimental data (MULLIN; MERSMAN, FOSTER). Therefore, we decided to conduct a comparative study of these techniques using KHT solutions as the testing material. Working with a specially designed apparatus we have simultaneously determined the nucleation time of KHT aqueous solutions using the following methods: a) visual determination, b) variation in transmittance, c) variation in reflectance, d) variation in conductivity and e) variation in pH.

2. Experimental

2.1. Description of the apparatus used for the measure of the induction time

Essentially the apparatus is made up of three areas (Fig. 1).

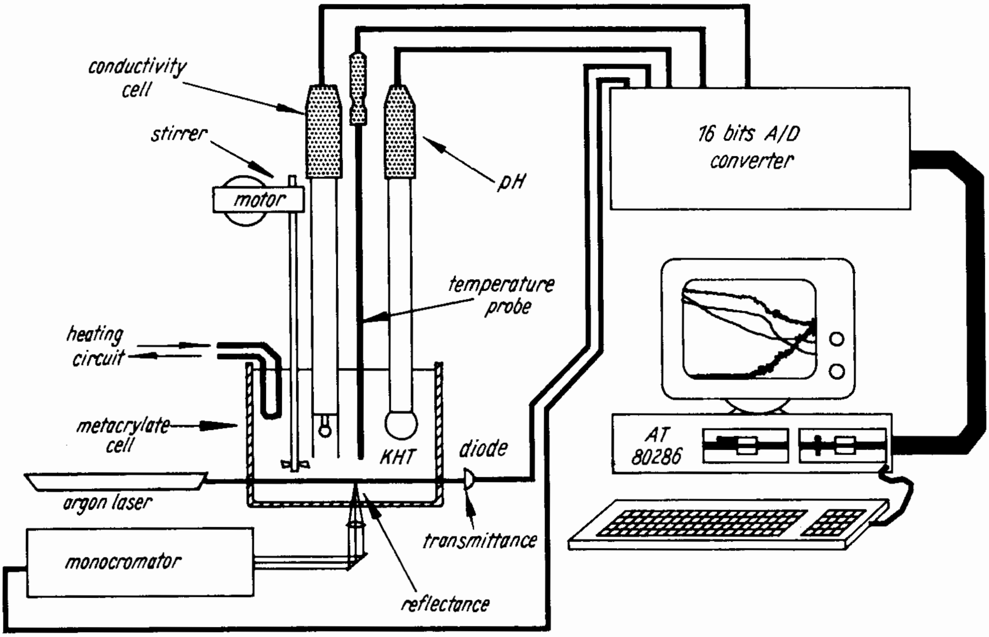

Fig. 1. General view of the apparatus. a) Precipitation cell, b) Light source and external detectors, c) Storage and analysis of data

a. Precipitation cell

The precipitation cell is a cube with a volume approximately equal to 64 cm^3. It is made from metacrilate. A teflon coil of about 3 mm in diameter is placed inside and connected to a thermostatically controlled water source which allows control of the cell temperature. The solution can be homogenized by the use of a stirrer designed in such a way that does not allow the formation of bubbles within the solution to be studied.

The cell also contains a pH sensor connected to a pH-meter Crison model 2002 with automatic temperature compensation, an electrode for measuring conductivity (cell constant of 1.0 or 0.1 cm) connected to a conductivity meter Crison model 522 and, finally, a temperature sensor type K.

b. Light source and external detectors

The growth cell is trasversed by a beam of light coming from an Argon (Ar^+) laser source with a power of about 100 mW. This radiation is used for the visual method and for the quantitative detection of the transmittance and reflectance. The transmitted radiation through the cell is detected by the plate of an encased transistor (2N3035), with its shell being cut leaving the transistor plate to be treated as a photovoltaic point cell (a square with less than 0.5 mm per side). Additionally, the emission of diffuse light at a 90 degree angle with respect to the direction of the laser beam light is collected through an optical system which permits the cancellation of the Rayleigh diffusion. Finally, the diffused light is analyzed with a double monochromator, tuned to the laser frequency, using as detector a photomultiplier mounted on a system for the counting of photons. For the visual method operation is done with a push-button which is connected directly to the computer.

c. Register area

The analog output made available by the external and internal sensors are routed to a 16 bit A/D converter, custom designed by INFESA w digital output received by an AT 80286 type microcomputer where data are stored for later analysis.

2.2 Software

We have generated a computer program called QBSAD for the taking and analysis of data. The program has more than 1600 lines of code and is written in QBASIC already compiled. The program controls the frequency in the taking of data up to a maximum of 20 data input per second per channel. The program also allows to trigger the taking of data when a particular event takes place, usually when the temperature is close to precipitation (for instance, the saturation temperature). Data can be obtained in a common mode or in a differential mode and can be taken and stored in point for or temporarily averaged. This program also provides capabilities for mathematical manipulation of data such as smoothing (which can be achieved by several methods), numerical derivative calculations of the obtained curves, and noise analysis of the detected signal.

2.3. Sequence of events of the experiment

The experimental protocol is as follows: an amount of KHT and the required amount of solvent to prepare a saturated solution at temperature T_e above the ambient temperature is poured into the cell. The temperature of this solution is raised by a temperature t_0 above the temperature of saturation to insure that the KHT has been completely dissolved. Once this has been verified by checking the stability of the signals from the different sensors, the solution is left to cool following the natural law. When a predetermined temperature is reached which is close to the expected precipitation temperature, the trigger for the taking of data is activated, maintaining this activity until the precipitation point is past by a wide margin.

Aqueous solutions of KHT made with distilled water and filtered KHT through a sieve of 40 μm were used in all the experiments.

3. Results

Each of the data set recorded with the previously mentioned techniques are graphically displayed and later analyzed by following two criteria: a) the tendency of the data and b) the noise superimposed over that tendency. To study both characteristics the developed software allows the use of mathematical methods such as:

a) Obtaining the derivative, which is accomplished by linear adjustment within a given interval of points and a later calculation of the slope.

b) Smoothing techniques. These include standard techniques as well as the possibility to collect averaged data, i.e. data with a value corresponding to the average of a set of n consecutive inputs, where n is an automatically adjusted value by the computer and is a function of the maximum speed in the acquisition of data and the real frequency set for the particular experiment.

c) Noise analysis. This requires to work with an odd interval of data ($2n + 1$), which are averaged, calculating afterwards the typical deviation of the central datum.

Figure 2 shows a set of data obtained with the apparatus described above and using the different techniques that were tried. The data belong to experiments performed with a solution of 0.96 g of KHT in 65 cm^3 of distilled water with a trigged temperature set at $T_t = 37\ ^\circ\mathrm{C}$. Newton's cooling law was adjusted by a high-temperature boundary of $T_e = 49\ ^\circ\mathrm{C}$, a low-temperature boundary of 28.8 °C and a coefficient of thermal decay of $-5.78 - 10^{-4}\ \mathrm{s}^{-1}$. The frequency in the taking of data was $4\ \mathrm{s}^{-1}$.

3.1. Analysis of the signal from the visual method

In this widely used method an operator visually detects the clouding of the solution produced by the process of precipitation. At the moment that the process of precipitation is initially detected by the operator, a switch is activated by him producing an electrical signal received

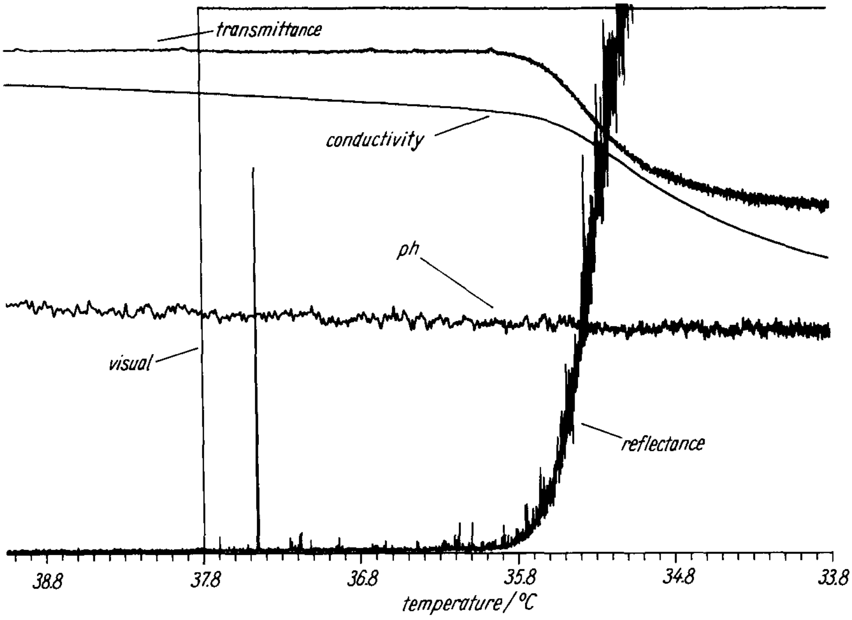

Fig. 2. Experiment PKHT10. Global visualization of all signals. Characteristics: total numbers of data points per channel: 3000. Scan data: 2 points/second/channel. Laser beam: 0.02 watt $W_0 = 19436.6\,\mathrm{cm}^{-1}$

by the computer and entered into the experimental sequence. The value obtained by this technique depends strongly on the skill of the operator. This method was tested for different degrees of the expertness of the operator in the detection of the salting-out. The operator received repeated training in the observation of the precipitation of KHT in order to obtain finally data equivalent to that of any specialist. In the best case and thanks to the presence of the laser radiation, which made possible the visualization of the first shining coming from the forming crystallites, it was determined that salting-out took place at a temperature of 34.65 °C

3.2. Analysis of the transmittance signal

This signal, along with the reflectance, forms the most complex set of data to analyze. In order to clarify the analysis of the intensity, Figure 3 shows the smoothed transmittance signal and the noise associated to it. The average intensity of the transmitted light clearly shows a strong variation associated to the process of phase transition. It permits to identify a singular point for the detection of the first crystals in the solution. Moreover, when analyzing the behaviour of the noise, it can be observed that it maintains a constant level until a certain time at which starts rising uniformly up to a new value at which it stabilizes again. Such a behaviour clearly belongs to the beginning of the formation of nuclei and subsequent crystal growth. A detailed analysis of this variation in the noise associated to the intensity of the transmitted beam could lead one to informations on the kinetics of nucleation and growth processes and the evolution in time of the crystal size distribution. Meanwhile, the very existence of noise led us to detect the formation of the solid phase with a better sensitivity. Thus, the temperature of detection for the precipitation point was 34.25 °C, and 35.05 °C for the tendency and the noise analysis, respectively.

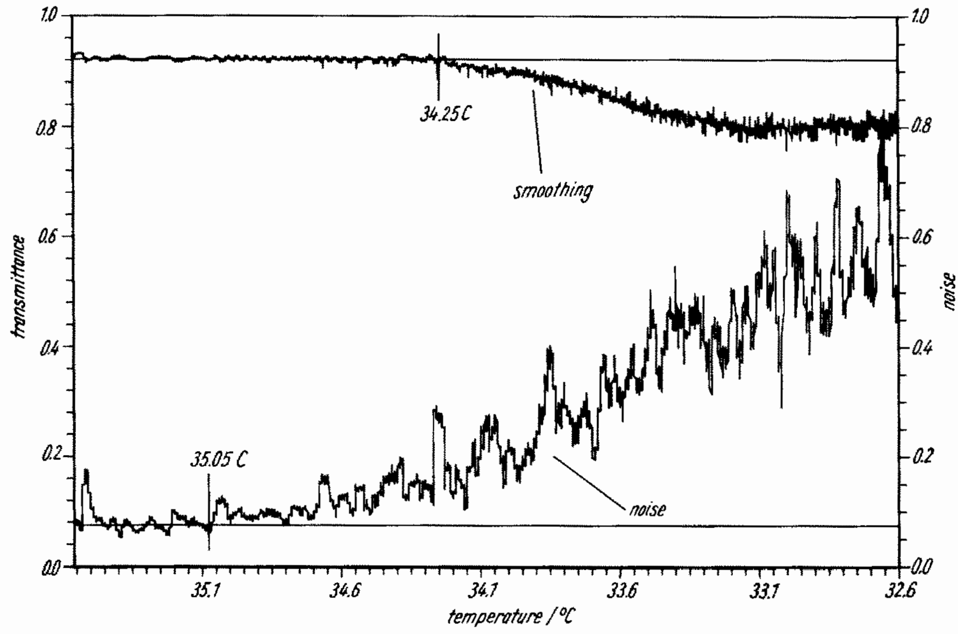

Fig. 3. Experiment PKHT11. Analysis of transmittance (smoothed signal and noise). Smoothing function: mean value over two points for 30 scans. Noise: central point deviation for 41 data interval

3.3. Analysis of the reflectance signal

The discussion applicable to this signal is the same as that one for the analysis of transmittance (Fig. 4). The detected signal in this case is the reflection of the laser radiation of the sides of the forming microcrystals. A powerful and very sensitive system of photodetection (a spectrometer normally used for Raman spectroscopy), with high localization detects the reflected photons by the forming nuclei. To avoid the bottom of the signal coming from the light emitted by Rayleigh diffusion, an analyzing filter is placed in the collector's optical system which takes advantage of the strongly polarized emitting properties of this signal, practically eliminates it. The study of the noise variation in this case provides the most sensitive record of the precipitation. Thus the temperatures of detection for the variation of tendency and the variation of the noise are in this case 34.70 °C and 35.20 °C, respectively.

3.4. Analysis of the conductivity signal

The signal of conductivity is very clean (Fig. 5), even without taking data with temporary averaging. This is due to the fact that the distance between the plates of the sensor is several orders of magnitude larger than the size of ions causing the conductivity, and consequently the obtained record is a special average of the possible inhomogeneities of the solution. The tendency shows clearly the decrement in conductivity as a result of the process of nuclei formation, justifiable theoretically because of the lowering in the number of ions in the

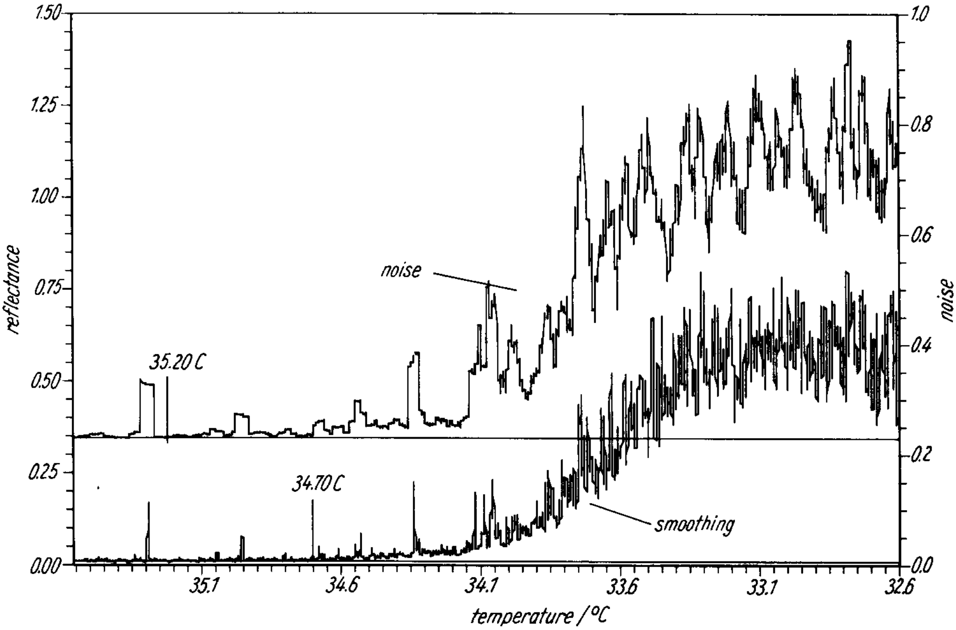

Fig. 4. Experiment PKHT11. Analysis of reflectance (smoothed signal and noise). Smoothing function: mean value over two points for 30 scans. Noise: central point deviation for 41 data interval

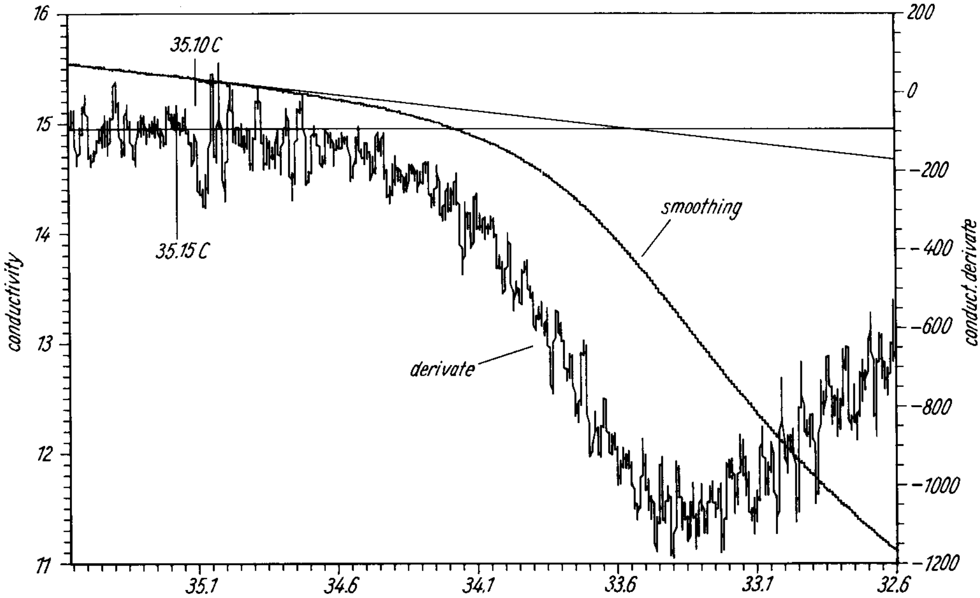

Fig. 5. Experiment PKHT11. Analysis of ionic conductivity (smoothed and derivative signal). Smoothing function: mean value over two points for 30 scans. Derivative: linear regression for 31 data interval

medium. The cleanlines of the signal allows the derivative as the only mathematical treatment for increasing the sensitivity. The detection of salting-out with the variation of the tendency as well as from the derivative curve permits its localization at a temperature of 35.15 °C and 35.10 °C, respectively.

3.5. Analysis of the pH signal

Although theoretically this signal did not hold very much promise for the case of KHT solutions, it was decided to perform a routine check considering that it may be of interest in the future use of this apparatus with other systems of precipitation. The evolution of the pH signal which was obtained in separated experiments (one of them is shown in Fig. 2), appears with an almost constant value, even after precipitation has taken place, not registering therefore any substantial variation in any of the detection criteria at the instant of precipitation. As was indicated, this stability of the pH value versus the precipitation was expected theoretically and therefore in the specific case of KHT solutions cannot be used as a technique for detection of nuclei formation.

4. Discussion

Table 1 shows the values of the metastable zone width and differential induction time obtained through the different methods tested in this work. From these it can be concluded that the most sensitive method for registering the precipitation is the noise analysis associated with the signal of the reflected beam intensity. Considering the value obtained with this technique as a reference, the delay times of each of the others are indicated as t_i. Note that the second most sensitive technique is the conductivity, ahead of the analysis of noise associated with the transmittance. Due to its availability and easier use, conductivity is therefore the technique best suited for situations where the reflectance cannot be recorded. Note that the delay time for conductivity in relation with reflectance is 1/10 of a degree and that the supersaturation when precipitation takes place in the thousands.

Table 1
Delay time, temperature of salting-out and supersaturation values detected with the techniques studied. Signal: slope signal analysis. Noise: noise signal variation. Derivate: Slope analysis using the first numeric derivative. T_p: measured temperature in the precipitation point. t_i: delay time with respect to the most sensitive technique. C: supersaturation measure as $C_e - C_p$ in g/100 cm^3

Input method	detection	T_p	t_i	C
visual	signal	34.65	155	0.568
transmittance	signal	34.25	278	0.581
transmittance	noise	35.05	41	0.555
conductivity	signal	35.15	14	0.552
conductivity	derivate	35.10	27	0.554
reflectance	signal	34.70	141	0.566
reflectance	noise	35.20	0	0.551
ph	There is no significative variation			

The visual determination of the nuclei formation, a common practical technique, increases appreciably the value of t_g. Even in a case like ours, where the observation is enhanced by the presence of laser radiation, the precipitation is detected two minutes later in relation with the conductivity technique and with a difference in temperature of more than one degree. As it was expected, these values are similar to those obtained directly from the reflectance data, since as a matter of fact, the human eye is detecting this property. Considering that in addition to the delays which were measured, the data obtained by visual method are of a subjective nature and depends upon the experience and degree of attention of the operator, we plan to disregard this technique for future studies on precipitation behaviour.

Induction time and metastability zone width are experimental data widely used in the evaluation of fundamental kinetic parameters in industrial crystallization. Our data, obtained simultaneously with several techniques, clearly show that the differences between them are large enough to be considered in such kind of evaluations and that the data reported on the maximum available supersaturation, τ, and metastable zone width should be accompanied with the kind of technique used for the detection of the precipitation point.

Lastly, the analysis of the evolution of noise associated with the intensity of the transmitted and reflected beams can generate information not only on the values of τ, but also on the evolution of the crystal size distribution during the precipitation process. This analysis, based on a computer simulation of the evolution of the theoretical transmittance as a function of a random distribution of particles in a tri-dimensional space, will be published separately.

5. Conclusions

An apparatus has been built and fine tuned for the measurements of the metastability zone width and induction time. This equipment allows simultaneous measurements of these variables by different techniques which involves electrochemical properties and optical properties of the solution under study. Our results, applied to KHT solutions, clearly indicate that the signal due to the optical reflectance and particularly the inherent noise within it, is together with the signal due to conductance the most sensitive variable for the precipitation and as such minimizes the value of the parameter t_g described above.

This work has been performed under financial support from CICYT Project number PA86-0119.

References

DE JONG, E. J.: Industrial Crystallization 78, Amsterdam 1979
JANSE, A. H., DE JONG, E. J.: Trans. IChemE. **56** (1978) 187
MERSMAN, A., FORSTERS, W.: Industrial Cristallization 84, Amsterdam 1984
MULLIN, J. W.: Crystallization, London 1972
NÝVLT, J.: Progr. Crystal Growth and Charact. **9** (1984) 335

(Received June 20, 1990, accepted
July 3, 1990)

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