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Evolution of Optical Transmittance in Precipitants Solutions. A Computer Simulation

We present a computer simulation model of the evolution of the transmitted light intensity traversing a reservoir that contains a supersaturated solution. From the analysis of the noise associated with the main signal, it seems to be possible to differentiate whether mass precipitation occurs by homogeneous nucleation or by pure crystal growth.

1. Introduction

The use of light-scattering techniques for the characterization of particles size (ELIÇABE, GARCÍA-RUBIO (a, b)), and even particle size evolution (DAVEY et al.), is a promising technique on particle characterization, in both, aerial and solution environments. However, it is not yet clear if these methods can be used in quantitative studies for the characterization of nucleation kinetics, which, has been made traditionally by sieve analysis (TOSCHEV et al.; NÝVLT et al.; NÝVLT; SÖHNEL, MULLIN; NÝVLT, ŽÁCEK; HOSTOMSKÝ). The problems mainly appear when experimental procedures, needing on line data acquisition, are carried out.

Recently (MARTÍN et al.), in a comparative study of the different techniques used for the detection of salting-out we had observed the potential interest of the transmitted light signal and its associated noise for the characterization of the precipitation kinetics. Because of the low cost and technological simplicity of the technique, we though to be worth to explore that potential use. In consequence, the aim of this paper is to test the possibility to distinguish between the occurrence in salting-out solutions of nucleation (i.e., the formation of new particles) and/or crystal growth processes (i.e., the size increment of the particles in the system), from the information obtained by recording transmitted light intensity.

2. Experimental

A common experimental method for the detection of salting-out is to measure the transmittance of a laser beam after traversing a reservoir containing the solution to be tested. A typical arrangement is displayed in Figure 1 (see MARTÍN et al. 1991, for full experimental description). In that case, a laser beam of 0.1 W and wavelength of 514.5 nm is focused on the core of a reservoir of 64 cm^3 in volume containing a solution which is carefully stirred in order to avoid bubbles formation. Hence, particles of solid to be formed will be homogeneously dispersed and therefore the local concentration of particles in the volume under beam will be representative of its concentration in the bulk. A photodiode placed outside the cell on the beam path (working as a beam-catcher) records the intensity of the transmitted light which is later digitized and analyzed by computer. Figure 2 shows a typical output of the variation of the transmitted light intensity and the noise associated to it versus temperature decay.

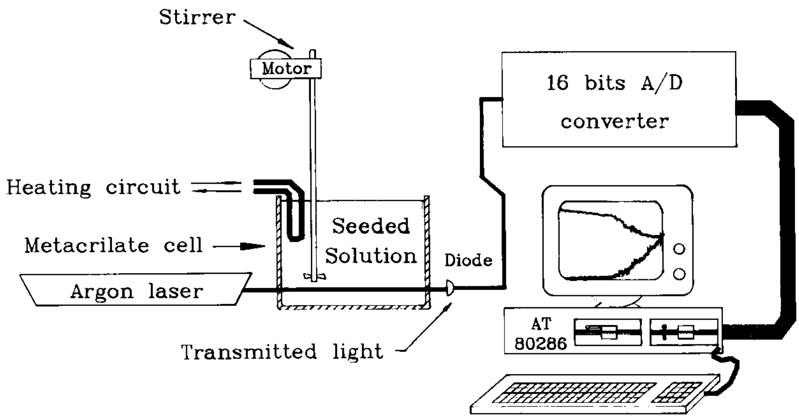

Fig. 1. An experimental set-up for the measurement of the transmitted light intensity

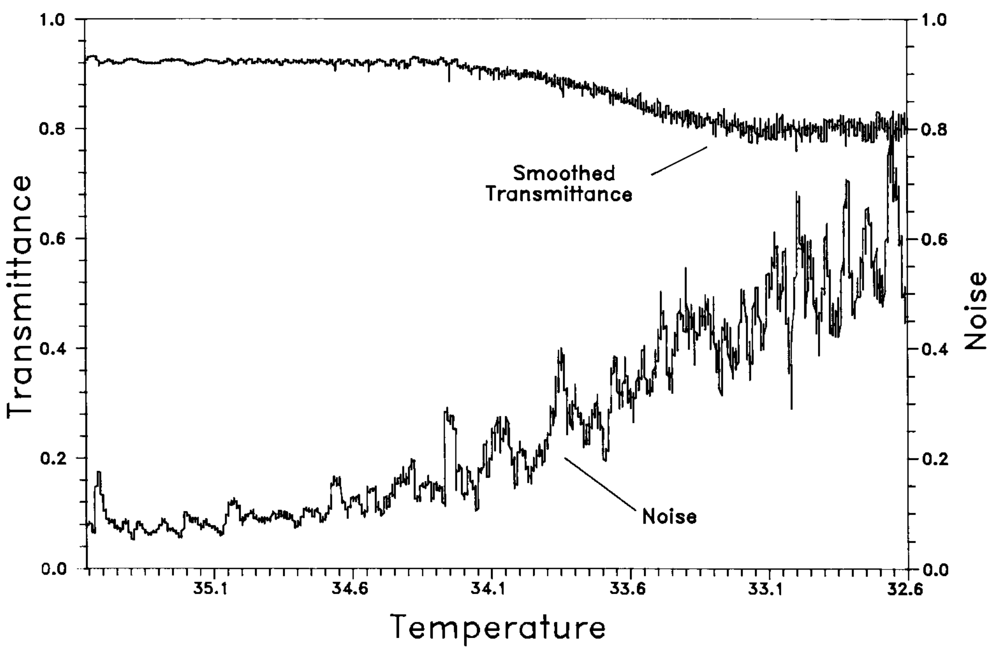

Fig. 2. Typical output of the variation in time of the intensity of the laser beam (a) and the noise associated to it (b)

3. Computer simulation

In the computer model we consider a volume with an initial amount of spherical particles equally sized, similar system to a seeded solution. From this, we have studied the behavior of the intensity of a laser beam, traversing it, when an evolution of particles occurs. The effect is similar to a mass precipitation in a supersaturated solution.

In order to simplify the process, only two basic evolution of particles have been simulated:
a) Pure nucleation in which the precipitate takes the form of new spherical particles, equals to the previous existing.
b) Pure crystal growth, in which the number of particles is constant but they are increased on their size.

For a best following of physical and mathematical descriptions, we need to use the next notation:

V_c	volume of the cube cell
V_b	cell volume under laser beam
S_0	surface of output observed radiation
R_0	radius of the S_0 surface
M_p	total precipitated mass
N_p	total number of particles in the cell
N_b	number of particles under laser beam
V_p	absolute volume of the particles
S_p	absolute hiding surface of the particles
R_p	absolute radius of the particles
S_h	relative hiding surface of the particles
R_h	relative radius of the particles
T	transmittance value (%)
S_n, S_i	total hidden surface by n or i particles
t	experimental time.

We start with a random number of particles N_p, characterized by their cartesian coordinates, X, Y and Z (ranging from +2 to −2) with the origin in the center of the growth cell. Therefore, all the particles will be inside a cubic cell. Next, we consider the common volume V_b defined by the cell and the geometrical representation of a laser beam traversing it along the −Y, Y direction.

When traversing the X−Z back face of the cubic cell, the laser beam will illuminate a surface area S_0 of a photodiode placed on its trajectory. Assuming no particles in the cell the transmittance will be 100%. The random generation of particles will create an ill-defined number of particles N_b in V_b. Therefore, to measure the transmittance we will need to know the part of the laser beam section intercepted by the particles along the optical path. Each particle will intercept a surface S_p equal to the orthogonal projection of its volume V_p to the XZ plane and the amount of all particles contribution along the optical path is S_n. The ratio between $S_0 - S_n$ and S_0 is the transmittance value. In order to have a real simulation of the experiments we need to introduce several corrections:
a) Experimentally, we can use two types of geometry: unfocussed and focussed. If we use a unfocussed geometry, the trajectory of laser beam is cylindrical and the sample volume intercepted by this, is bigger than the particles grownded, then we can detect only an average signal from this interaction. In the other hand, we can use a focused geometry, in this case, the intercepted volume in focus is similar to grown particles and a noised signal is acquired. As we are interested in the study of signal to noise relation, the last case is preferred. The focussed geometry simulation is more complicate than unfocused because the trajectory around the focus is mathematically described by an hyperbole centered in the cartesian origin, i.e., in the center of the cubic cell. Two parameters characterize this geometry (Fig. 3.): $R(0)$, which is the radius in the focus, i.e., the minimum radius of the hyperbole

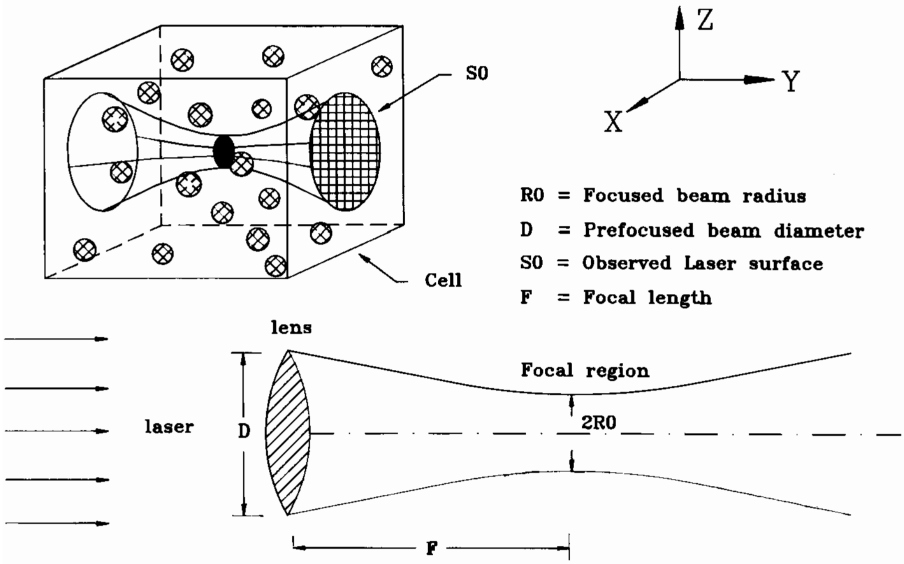

Fig. 3. Geometrical relations used in the computer simulation of the transmitted light through a solution

and $R(y)$ which is the radius at the distance y $(-2 \leqq y \leqq 2)$ from the focus. To calculate these two parameters, two relations are relevant:

$$R(0) = \frac{2F}{\omega\pi D} \tag{1}$$

and

$$R(x)^2 = R(0)^2\left[1 + \left(\frac{x}{\omega\pi R(0)^2}\right)^2\right] \tag{2}$$

where F is the focal length, ω is the wavenumber of the radiation and D is the diameter of the laser beam before focalization.

b) Due to focalization, the circular section of the laser beam (S_0) is a function of y displacement ($\pi \cdot R(y)^2$). In consequence, a factor must be included to correct the value of the ratio S_p/S_0.

c) The possibility of sharing X and Z values for two particles with different Y values is very high and therefore the total surface hidden by n particles cannot be calculated by the product $n \cdot S_p$, then a factor of shadow eclipses must be evaluated (Fig. 4).

d) Obviously, a shape factor should be introduced in many practical cases, in particular for elongated particles. This shape factor affects mainly the punctual noise associated to the signal but it has not effect to the mean intensity and to the noise averaged. Then, one can assume that, due to the random movement, the average surface hidden by a set of particles, whatever the shape factor, can be considered to be equivalent to the one produced by a set of spherical particles. Note that we are interested in the trend of the average noise associated to S_p and not to the absolute values of the variables to be measured. This is the reason why, in spite of the low number of particles for pure crystal growth simulation, no shape factor has been considered in the simulation. Thus, we will work with spherical particles along this study with their radii R_p as a characteristic dimension.

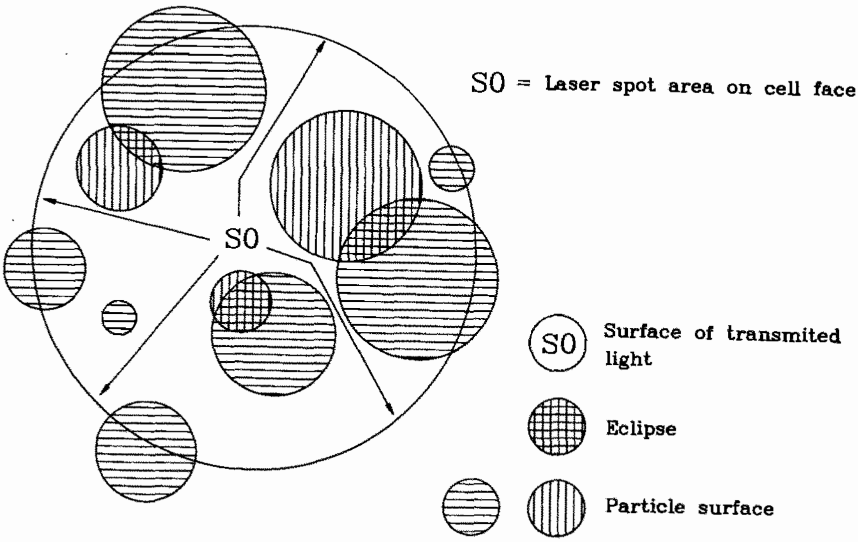

Fig. 4. Orthogonal projection on S_{ob} showing the shadows provoked by the particles. Note the effect of eclipses

e) We assume for the particles to have 100% absorbance, which may not be true. Such a partial opacity will affect only the absolute values of intensity and not the relations searched for in this study. The transmittance coefficient of the solid particles can be easily introduced by reducing the particle radius by an appropriate factor, that could serve as well to take in account the effect of diffraction phenomena, completely neglected in our simulation.
f) In pure nucleation, the size of new particles are constant and equal to that of the existing particles in the system. In all cases, no secondary nucleation is considered.

4. Results of computer simulations

The input variables of a computer simulation with the values chosen for our experimental set-up are shown in Table 1.

The results obtained are shown in form of dots in Figure 5. They belong to 10^3 iterations and the precipitated mass is increased for each iteration by an amount equal to a 0.5% of previous mass (Tab. 2). Thus a power law of growth has been used, but it no has significance on the final values.

Table 1
Input values in the computer simulation

$S_0 = 0.17\ mm^2$
$R_0 = 0.231\ mm$
Focal length = 6 cm
Wavenumber = 19436.3 cm^{-1}
Prefocus diameter = 1.5 mm
Edge of cell = 4 cm

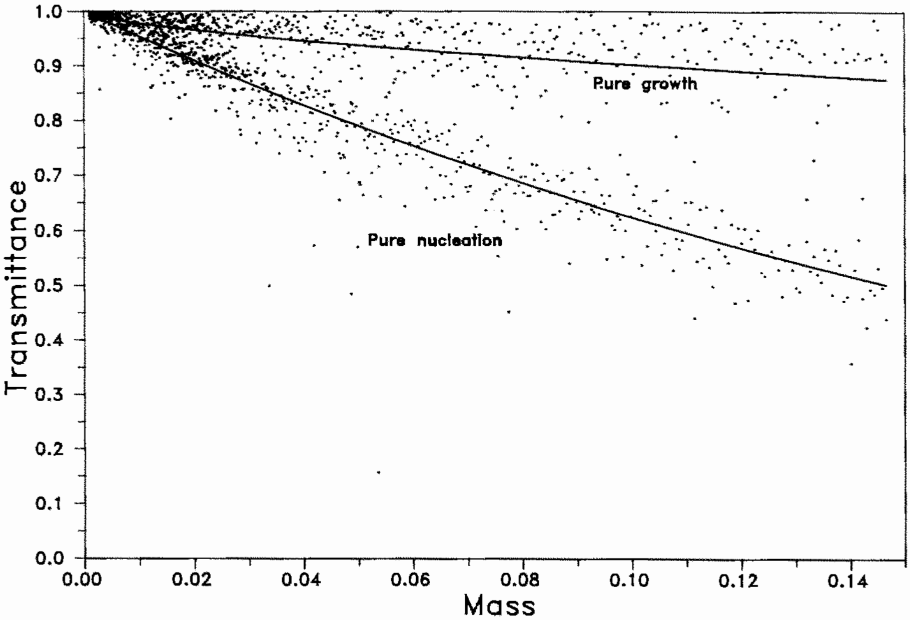

Fig. 5. The dependence of the transmitted light intensity on precipitated mass. Dots are the computer data outputs and full lines represent the analytical expression derived in the text

The dispersion of the transmittance data is due to the random generation of particles and to the fact that in the region in focus $R(0)$ is similar to R_p and therefore multiple intersections can produce such deviations. These deviations are the origin of noise and a mean value can be determined for each point. To proceed it, we have selected a set of specific values of the precipitated mass and, for them, we have obtained 500 values of transmittance and their standard deviation. The result of these last calculations are shown in Figure 6, which are the plots of transmittance versus noise. Clearly, pure nucleation and pure crystal growth can be characterized by well defined trends and the region in between belongs to experiments where nucleation and growth occur simultaneously.

Table 2
Evolution of main parameters belong the calculations. M_p in grams, R_p in μm, S_p in μm^2, N_p in particles × 10^3 and N_b in particles

Process		M_p	R_p	S_p	N_p	N_b
nucleation	from	0.0001	5.0	78.5	96	4
	to	0.0146	5.0	78.5	14040	579
growth	from	0.0001	5.0	78.5	96	4
	to	0.0146	26.3	2176.3	96	4

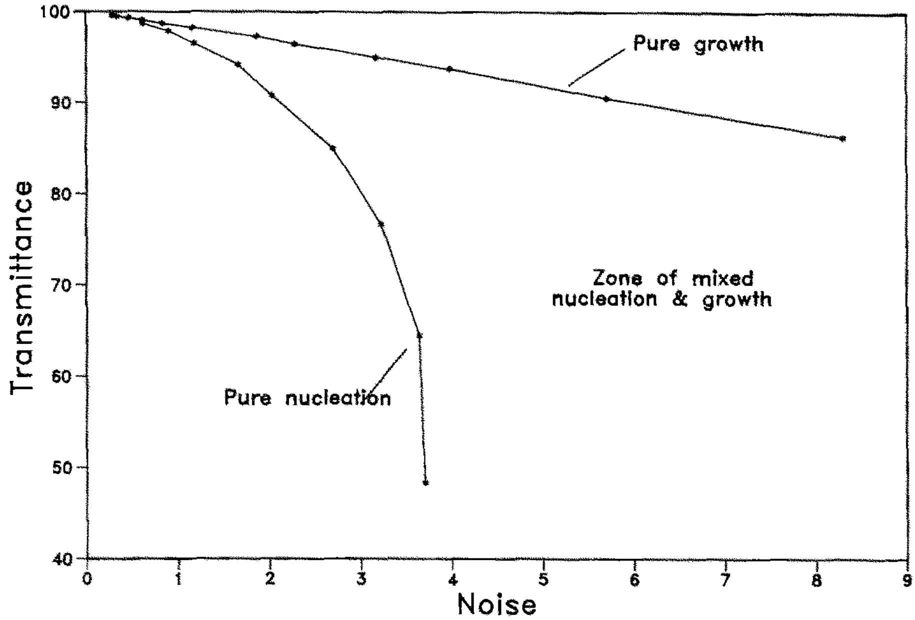

Fig. 6. Noise versus transmittance plots for pure nucleation and pure crystal growth process after computer simulation

5. Discussion of results

To explain the results by means of an analytical process, let us consider the number of particles intercepted by the beam to be N_b. The hidden surface projected be each particle onto the observation surface S_0 is

$$S_h = S_p \cdot F_p \tag{3}$$

where S_p is the specific surface of the particle and F_p is the correcting factor to the particle Y position. This factor can be obtained from the ratio between S_0 and the mean spot surface along the laser optical path. We have calculated this factor, with a computer program, resulting equal to 2.9837.

Let S_i be the orthogonal projection of N_i particles under V_b on the back X-Z face of the cell (Fig. 3). For $i = 0$, the area occupied by the spot on this face will be S_0. If we assume that all the transmitted radiation is received by the photodiode-situation easy to fulfill in practical experiments-, then S_0 is the area on the beam-catcher diode. For $i = 1$, the surface hidden by the particle is $S_{h1} = S_h$. Because of the enlargement of the volume under beam along the Z-axis, it is clear that several particles could share a subset of the $\{x, z\}$ coordinates defining their effective area. Therefore, for $i = 2$, the S_h value could be lower than the summation of the particles' effective areas. Assuming the probability of no-coincidence to be

$$P = 1 - \frac{S_{h1}}{S_0} \tag{4}$$

the total area hidden by two particles will be

$$S_{h2} = S_{h1} + S_h \cdot \left(1 - \frac{S_{h1}}{S_0}\right) \tag{5}$$

and for $i = n$ particles we have:

$$S_{hn} = S_{h(n-1)} + S_h \cdot \left(1 - \frac{S_{h(n-1)}}{S_0}\right). \tag{6}$$

In terms of transmittance, relation (6) can be written in the form

$$T_n = \frac{S_0 - S_{hn}}{S_0} = 1 - \frac{S_{hn}}{S_0}. \tag{7}$$

It is easy to demonstrate that the transmittance values obtained in (7) for $1 \leqq i \leqq n$ are the development of the Newton's binome

$$T_n = \left(1 - \frac{S_h}{S_0}\right)^n. \tag{8}$$

In our simulated study n is equal to N_b, the number of particles in V_b (Laser beam volume), and the relation (8) can be expressed in the form

$$\log T_n = N_b \cdot \log\left(1 - \frac{S_h}{S_0}\right). \tag{9}$$

When calculating a pure nucleation process, the volume of every one of particles is constant and, for the same reason, their hidden surface. Thus, transmittance values depend only on the number of particles, which is calculated by the relation

$$N_b = \frac{M_p V_b}{\varrho V_p V_c} \tag{10}$$

where V_c is the cell volume, M_p is the total mass precipitated, and ϱ the density of the solid particles. Because V_p, V_b, and V_c are constant, N_p varies linearly with M_p.

On the other hand, if exclusively crystal growth occurs, N_p is constant and V_p and S_p are variables. The dependence of S_p on the precipitated mass M_p is given by

$$S_p = \left(\frac{3M_p}{4\varrho N_p}\right)^{2/3}. \tag{11}$$

Note that if we substitute the relations (10) and (11) in (9) and if M_p is known (for instance by conductimetry) the decay in intensity associated to it can be predicted. These values of calculated transmittance are plotted in Figure 5 using full lines for both processes, nucleation and growth, and they fit well with the simulation output.

As shown in Figures 5 and 6, the variation of the transmittance as the amount of precipitate increases (Fig. 5) is clearly different for pure nucleation and pure growth. However, the difference between both kinds of process is still more evident by plotting transmittance versus noise (Fig. 6): we can see how the data for pure growth has a linear fitting and for pure nucleation has a non-linear fitting. Linear relationships of the transmittance with

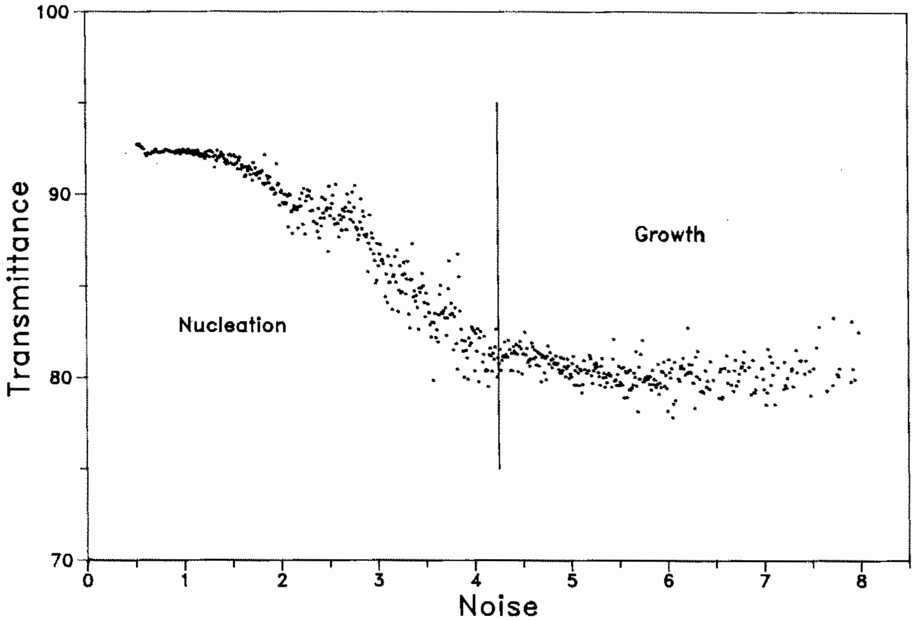

Fig. 7. Plots of experimental noise versus transmittance for data plots in Figure 2

their noise are expected to be observed in cases in which the growth of particles is the main process. Deviations from linearity leading to lower noise values mean the simultaneous growth and formation of particles. Finally, when the noise changes as a parabolic function of the intensity decay, it is explained just by the formation of new particles in the system.

Finally, let us observe in Figure 7 the result of an experimental determination of transmittance versus noise, carried out by precipitation of KHT (Potassium Tartrate Acid) in the conditions described in MARTIN et al. 1991. Two regions are clearly distinguished on the plot, whose interpretation as an initial process of pure nucleation and a final process of pure growth, is evident.

In consequence, the interest of the use of noise associated to the identification of the processes working in a mass deposition phenomenon, appears to be clear. Nevertheless, our model still considers particle generation in a very simplified form. Therefore, we are currently working in the design of a less constrained nucleation model to be implemented into the simulation.

6. Conclusions

Data of transmittance values and their associated noise can be used as an interesting tool in order to differentiate whether in a given system, the increase of mass is released by the increment of the number of particles of a giving size or the increment in size of the already existing particles in the system. Such an analysis is particularly useful in the in situ characterization of the precipitation kinetics of seeded solutions, where the existence of homogeneous nucleation or particles growth have to be distinguished.

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