

Comparative Research of Silver Halide Tabular Crystals Formation Processes During Fine Emulsion Physical Ripening and During Gel Aging

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Introduction

Traditionally for creation of silver halide tabular crystals use a method of a control double-jet crystallization or method of physical ripening of fine emulsion. The process of tabular crystals formation in the latter case was investigated and the mechanism was offered. However formation of such crystals can proceed not only in an emulsion, where the mobility of microcrystals is not limited, but also with aging of containing fine microcrystals gelatin gel.

The technique of reception of tabular crystals was offered by means of fine microcrystals recrystallization in gelatin gel[1]. In this case the received fine emulsion was cooled down to temperature of gel formation and was maintained during 48-240 hours at the temperature 19±1°C. The authors investigated influence of conditions controlling the solubility of silver halide on process of tabular crystals formation in gel. It was shown that the efficiency of tabular crystals formation largely depends on of an initial fine emulsion microcrystals concentration in gel, and that the formation of tabular crystals proceeds at 19 °C, but its will not be formed at temperature 10 °C even during long (more than 800 hours) aging. The authors connected the observable phenomena that the growth of tabular crystals proceeded on the coalescent mechanism. In our opinion a large scientific interest is in more detail to study the process of tabular crystals formation in a gel. We undertook attempt to reveal laws and driving forces ensuring formation of silver halide tabular crystals during recrystallization in gel.

Experimental

At the first stage the fine silver halide emulsion was created. The synthesis was carried out in a following manner: An aqueous gelatin solution, containing 200 ml of distilled water, 6 g of photographic inert gelatin and 0.024 g of KBr, was placed in reaction vessel, and the temperature thereof was kept at 40 °C. To a vessel while stirring an aqueous solution of silver nitrate (1 mol/l) and aqueous solution of potassium bromide (1 mol/l) were simultaneously added thereto over 3 minute at a rate of 15 ml/min according to a double jet method. During addition pBr value was kept at pBr=3.2±0.2. The resulting emulsion contains isometric silver bromide microcrystals with average size 50 nanometers.

The received emulsion was used for creation of silver halide tabular crystals by a method of physical ripening and recrystallization in gel. The experiments have carried out in a following manner: to a gelatin solution (3 % gelatin) in glass tube at temperature 40 °C was added the necessary volume of a fine emulsion. Then the received mix during 5 minutes was cooled down to temperature 12 °C for gel formation. The received sample was maintained at room temperature 18±2°C during 72-500 hours. The dispersion characteristics of received microcrystals was estimated on photos received on an electron or optical microscope. During experiment the concentration of microcrystals of an initial fine emulsion, concentration and type of complexing ions, concentration of a gelatin etc were varied.

Calculations

Concentration of microcrystals in gel and in an emulsion was determined on the formula [2]:

$$[MC] = 6 \times 10^{12} \times \frac{[AgHal] \times M_r}{\pi \times d^3 \times \rho} \quad (1),$$

where [MC] - microcrystals concentration in emulsion (1/l);
[AgHal] - silver halide concentration in emulsion (mol/l);
Mr - molar weight of a silver halide;
d_{MC} - average diameter of microcrystals of a fine emulsion (nm);
ρ - density of a silver halide (g/cm^3).

On a figure 1 the dependence of concentration of microcrystals with the average size of 50 nm on a silver halide concentration is presented.

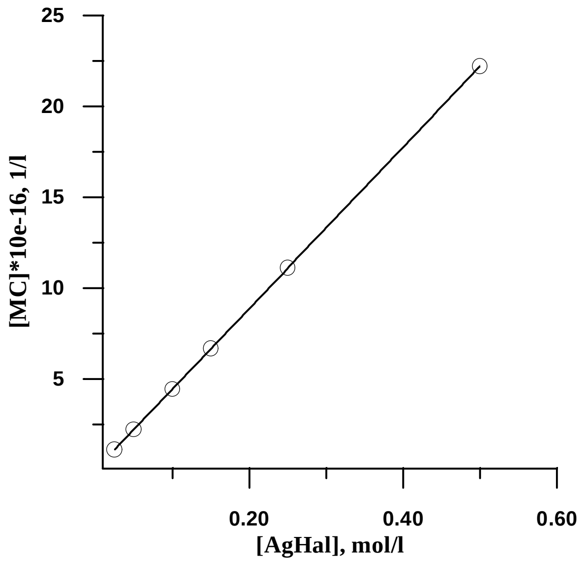

Figure 1. The calculated dependence of microcrystal concentration in gel on silver halide concentration (microcrystal size is 50 nm).

From general reasons, it was possible to expect that the essential influence on process of formation of tabular microcrystals can render distance between microcrystals in gel. If these microcrystals are distributed in gel in regular intervals, the average volume of environments per one microcrystal will be equal:

$$V_g = \frac{1}{[MC]} \times 10^{-3} \quad (2),$$

where V_g - gel volume per one microcrystal (m^3);
[MC] - concentration of microcrystals in gel (l^{-1}).

This individual volume can be presented as correct cube with an edge length:

$$l = \sqrt[3]{V_g} \times 10^9 \quad (3),$$

where *l* - cube edge length (nm);
V_g - gel volume per one microcrystal (m^3).

Considering the microcrystal size the average distance between particles will be:

$$l_{ip} = l - d_{MC} \quad (4),$$

where l_{ip} - average interparticle distance particles in gel (nm);
d_{MC} - average size of microcrystals of a fine emulsion (nm).

On a figure 2 the calculated dependence of interparticle distance in gel on concentration of a silver halide for microcrystals with the average size of 50 nm is presented.

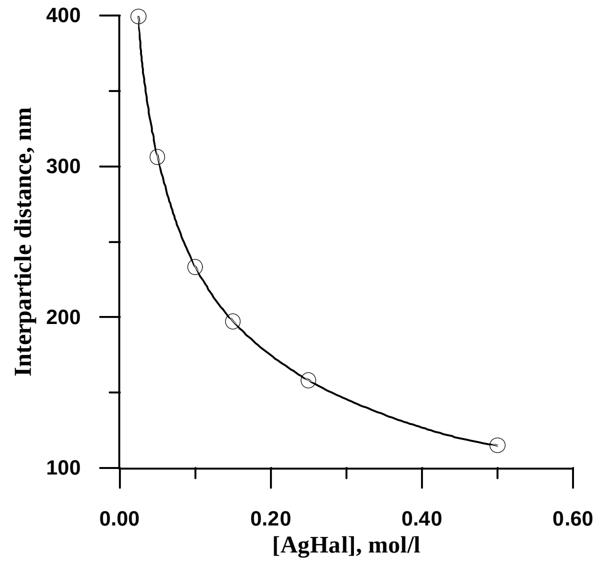

Figure 2. The calculated dependence of interparticle distance in gel on concentration of a silver halide (microcrystals average size is 50 nm).

The large importance on the dispersion characteristics of tabular crystals renders a quantitative ratio between tabular crystal nuclei and common microcrystals in an initial fine emulsion. The tabular crystal nuclei are formed at a stage of synthesis of a fine emulsion, together with usual microcrystals at the expense of a coalescence of formed particles[3,4]. By varying conditions of a crystallization of a fine emulsion, it is possible to increase or to reduce a share of formed nuclei and thus to adjust amount and size of tabular crystals in an emulsion. On the base of the assumption that all nuclei as a result of physical ripening turn to tabular crystals and knowing the geometrical sizes of initial microcrystals and final tabular crystals, it is possible to determine, how many common crystals in a fine emulsion are necessary on one nucleus under the formula [4]:

$$N_{MC} = V_T/V_{MC} \quad (5),$$

where N_{MC}- amount of microcrystals per one tabular crystal nucleus;
V_T - average volume of the tabular crystal (μm^3);
V_{MK} - average volume of a microcrystal of a fine emulsion (μm^3).

Considering that the tabular crystal has the form of a disk and a microcrystal of a fine emulsion - form of sphere we receive:

$$N_{MC} = \frac{3 \times d_T^2 \times h}{2 \times d_{MC}^2} \quad (6),$$

where d_T - average equivalent diameter of a tabular crystal (μm);
h - average thickness of tabular crystals (μm);
d_{MC} - average diameter of microcrystals of a fine emulsion (μm).

On a figure 3 the designed dependence of necessary amount of microcrystals of a fine emulsion with the average size of 50 nm per one tabular crystal with thickness of 100 nm on an average equivalent diameter of this tabular crystal is presented.

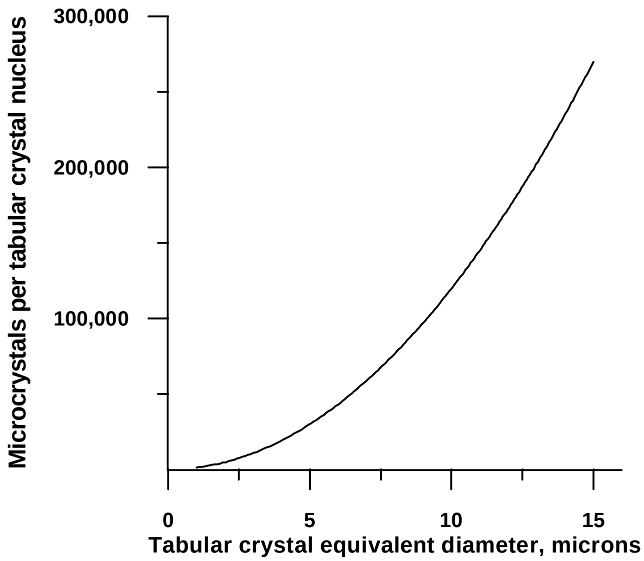

Figure 3. The calculated dependence of amount of microcrystals of a fine emulsion per one tabular crystal on an average equivalent diameter of this tabular crystal (microcrystal size is 50 nm, tabular crystal thickness is 100 nm).

The nuclei ratio in a fine emulsion was expected from the dispersion characteristics of tabular crystals received as a result of physical ripening of this fine emulsion. In case of ripening, the movement of microcrystals is not limited and all of them can take part in growth of tabular crystals.

Experimental Results

On the basis of result of experiments on research formation of tabular crystals during physical ripening of fine emulsion the conclusion was made that the formation of tabular crystals includes stages of transformation of a nucleus in a tabular crystal on the ionic mechanism and growth of a tabular crystal occurs simultaneously on ionic and coalescent mechanisms.[5-7]

It was expected that at a recrystallization in gel it will be possible considerably lower the contribution of processes of a coalescence in formation of tabular crystals. This, in turn, should result in essential change of the dispersion characteristics of formed tabular crystals. However, this forecast has appeared not correct, though a number of unexpected results were received also. First of all, it was revealed that there is a very strong dependence of growth of tabular crystals in gel from concentration of microcrystals of an initial fine emulsion. On a figure 4 the microphotos of crystals received as a result of a recrystallization in gel with different concentration of initial microcrystals and as a result of physical ripening are presented.

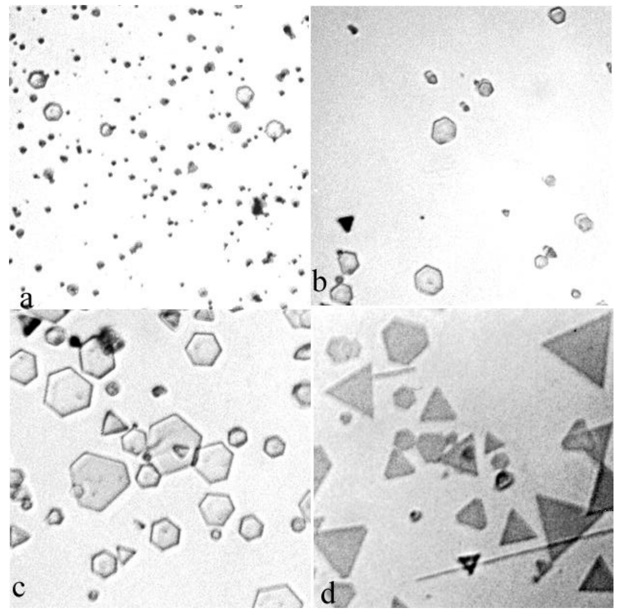

Figure 4. The microphotos (x1000) of crystal received by recry s-tallization in gel (pBr=1.0; gelatin concentration 3 %) and by physical ripening (d). The microcrystal concentration:
a - 1.11×10^{16} l^{-1};
b - 2.22×10^{16} l^{-1};
c - 2.22×10^{17} l^{-1};

On a figure 5 the graphic dependencies of an average equivalent diameter of tabular crystals on concentration of microcrystals in gel are presented. With reduction of concentration of microcrystals down to threshold value (1×10^{17} l^{-1}) the fast reduction of an average equivalent diameter of received tabular crystals and increase of a share of isometric crystals is observed. The very similar dependence was received by Breslav et al [1].

The influence on the dispersion characteristics is rendered also by concentration of a gelatin. On a figure 6 the dependence of an average equivalent diameter of received tabular crystals on concentration of a gelatin is presented. The increase of gelatin concentration makes the process of formation of tabular crystals less effective.

From the received results follows, that with increase of concentration of initial microcrystals and with reduction of gelatin concentration the number of microcrystals included in growing tabular crystals is increased.

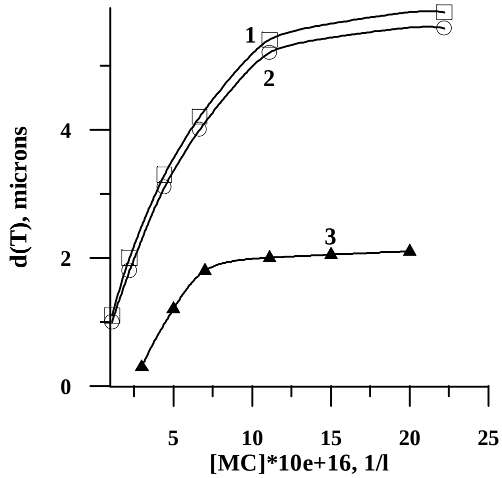

Figure 5. The dependencies of an average equivalent diameter of tabular crystals on concentration of microcrystals in gel. The initial emulsions characteristics:
1 - 76,000 microcrystal per nucleus, microcrystal size 52 nm;
2 - 73,000 microcrystal per nucleus, microcrystal size 50 nm;
3 - reference 1.

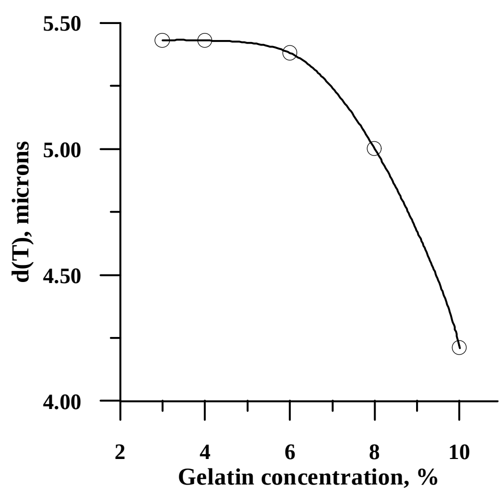

*Figure 6. The dependence of an average equivalent diameter of tabular crystals on concentration of a gelatin. The initial fine emulsion characteristics: microcrystal size - 52 nm, 76,000 microcrystal per nucleus, microcrystal concentration - 1.11*10 $^{17}l^{-1}$.*

It is represented expedient to enter concept about effective radius of action of a tabular crystal nucleus in gel. The fine microcrystals, which situated within of this radius take part in formation of a tabular crystal. If we know the amount of microcrystals per one tabular crystal and gel volume per one microcrystal, it is possible to calculate gel volume which tabular crystal growth supply:

$$V_{gel} = N_{MC} \times V_g \quad (7),$$

where V_{gel} - gel volume, ensuring growth of a tabular crystal (m^3);
N_{MC} - amount of initial microcrystals per tabular crystal;
V_g - gel volume per one initial microcrystal (m^3).

Then effective radius of action of a nucleus (r_{eff}, μm) will be:

$$r_{eff} = \sqrt[3]{\frac{6\times V_{gel}}{\pi}} \times 5\times 10^5 \quad (8)$$

The calculated values of effective radius of action of a tabular crystal nucleus are presented on figures 7 and 8.

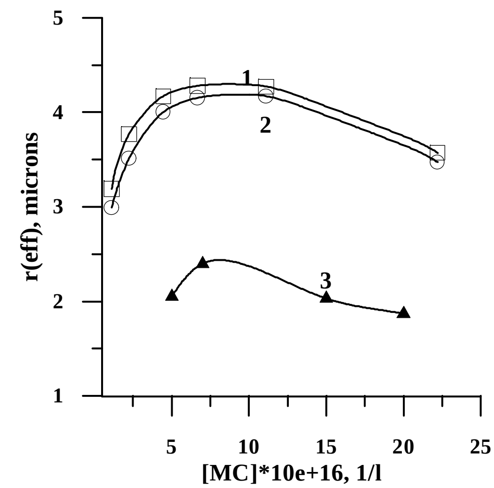

Figure 7. The dependence of effective radius of action of a tabular crystal nucleus on microcrystal concentration. The initial emulsion characteristics:
1 - 76,000 microcrystal per nucleus, microcrystal size 52 nm;
2 - 73,000 microcrystal per nucleus, microcrystal size 50 nm;
3 - reference 1.

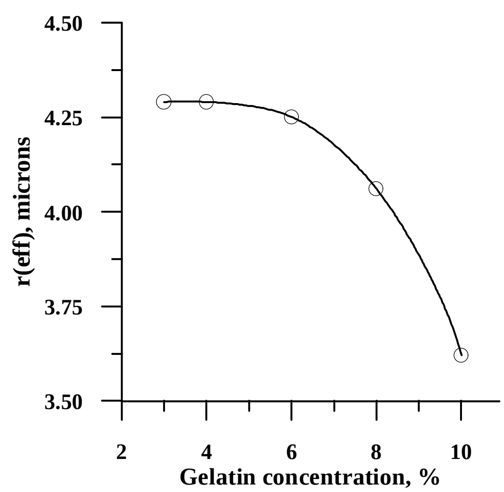

*Figure 8. The dependence of effective radius of action of a tabular crystal nucleus on gelatin concentration. The initial emulsion characteristics: microcrystal size is 52 nm, 76,000 microcrystal per nucleus, microcrystal concentration is 1.11*10 ^{17} l^{-1}.*

Discussion

In our opinion, the most probable reason of so essential changes of the dispersion characteristics of crystals, formed during a recrystallization, can be change of the mechanism of crystals formation in gel. It is very difficulty to explain observable dependence by increase of a diffusion way of ions. Experimentally was shown that the silver and bromide ions have rather high mobility in gelatin gel. Therefore hardly it is necessary to expect essential change of the dispersion characteristics of tabular crystals caused by the contribution of the ionic mechanism of growth. Thus most probable reason of change of the dispersion characteristics - change of amount of particles, which can supply growth of tabular crystals on the coalescent mechanism.

On the basis of the presented data it is possible to reach a conclusion, that initial microcrystals which are situated in sphere of effective action of a nucleus participate in growth of a tabular crystal mainly on the coalescent mechanism. The tabular crystals on this mechanism can be formed quickly, but the mobility of microcrystals in gel is limited also growth rate is limited by movement speed of the microcrystals. On the other hand, the mobility of ions in gel is high, but the growth rate on the ionic mechanism is small.

The opportunity of participation of an individual microcrystal on a coalescence process is determined by its size[6,7]. As a result of Ostwald ripening there is a change of the size of microcrystals and owing to high mobility of ions in gel the speed of this process depends on microcrystal concentration in a smaller degree. Through the certain interval of time in system does not remain of microcrystals capable to provide the growth of tabular crystals on the coalescent mechanism. After that the growth of tabular crystals on the coalescent mechanism stops. Thus, the radius of action of a nucleus will be always limited by speed of a microcrystals movement in gel.

On effective radius renders influence the gelatin concentration. The increase of this concentration result in appreciable reduction of speed of a microcrystals movement and in a smaller degree limits mobility of ions. In this situation effective radius of action of a nucleus decreases. If the amount of nuclei is great, the zones of their effective action are intersected and all microcrystals of a fine emulsion can participate in growth on the coalescent mechanism. After achievement of this situation the average equivalent diameter of formed tabular crystals does not depend any more on concentration of microcrystals of a fine emulsion and becomes close to value of an average equivalent diameter of tabular crystals received by a way of physical ripening. Thus, the final emulsion will contain tabular crystals with high crystallographic uniformity, as the share of isometric microcrystals is considerably reduced.

With reduction of concentration of microcrystals in gel, the situation can be achieved, when the contribution of the coalescent mechanism can be shown up to a zero level (see Figure 4a). In these conditions, the transformation of nuclei into tabular crystals on the ionic mechanism is observed. However as the growth on the coalescent mechanism is excluded, the tabular crystals do not have advantages over isometric crystal in growth rate. Therefore mix of tabular and isometric microcrystals of the approximately identical size at the end of recrystallization will be formed.

References

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