Investigation of Kinetics of Recrystallization of Silver Halide Microcrystals by a Turbidimetric Method

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Abstract

The method of recrystallization of fine emulsion is widely utilized in modern technologies of manufacturing of silver halide materials. However theoretical bases of the given method till now are investigated insufficiently. In this situation the essential contribution to clearings the mechanism of process could have the data on kinetics of a dimensional change of particles during recrystallization and dependence of this kinetics on conditions of carrying out of experiment. Besides the additional information can be obtained at comparison of results of recrystallization in a melted emulsion, and in medium of gel, where the mobility of crystals is restricted.

We carried out examination of kinetics of recrystallization of microparticles of silver halide on model systems in gelatin gel. The check of the size of microcrystals was made by a turbidimetric method. The dependencies of growth rate of crystals on distance between interacting particles and from distinction in a size of these particles were obtained. The experimental data allow in more details to study driving force and mechanism of process of recrystallization.

Introduction

The photographic emulsion used in technology of manufacturing of silver halide photomaterials represent the systems of a colloid type consisting of silver halide microcrystals with the size in an interval of 50-1000 nm, which dispersed in medium of a protective colloid (gelatin). Now to most widely used methods of synthesis of emulsions it is possible to attribute a way of a control double jet crystallization and way of a physical ripening of fine emulsions. There is the common opinion that during double jet crystallization the continuous neoformation of microcrystals of a silver halide takes place, which serve a material for growth of larger crystals[1]. In the most perfect techniques of synthesis these two processes are divided spatially[2]. Thus the key processes during a mass crystallization is the process of a recrystallization, i.e. transformations of finer crystals into larger in closed (physical ripening) or open (double jet crystallization) systems. The understanding of the mechanism and driving forces of process of a recrystallization would allow to solve a wide range both technological, and fundamental problems of modern photographic and colloid chemistry.

The method of a physical ripening is more suitable for research. In this case processes proceed in the closed system, which gives in to the description more easy. However in classical process of a ripening the processes of a mass transfer at an ionic level mask by moving of microcrystals owing to agitation and thermal motion. For understanding of laws of a recrystallization at a microlevel it is necessary to isolate the components of process of a mass transfer caused by moving of ions through a solution and by movement of crystals in system. The given task can be solved if to compare the process of a common physical ripening with agitation and the process of a recrystallization in gellike medium, where the movement of microparticles is impossible owing to steric obstacles of gel structure[3-5].

The great difficulty is represented with the control of change of the size of particles during a recrystallization. The method, which allows at the minimal intervention in system to ensure definition of an average diameter of growing particles and reduction of concentration of fine microcrystals is the spectral turbidimetry, based on the phenomenon of light scattering by colloid systems[6]. The method of an electronic microscopy differs by high labor input and is poorly suitable in this case because of parasitic processes of a recrystallization at a stage of preparation of replica of emulsion microcrystals.

The method of a specific turbidity is widely used in modern researches of processes of formation and growth of silver halide microcrystals[7-10]. However in all these researches the size of microcrystals was in the field of performance of the Rayleigh law for light scattering by small particles. It is accepted to believe that the equation of the Rayleigh is carried out, when the size of light scattering particles does not exceed $0{,}1\ \lambda$ - length of a light wave[6]. Thus limiting size of crystals for researches in a visible range of light should not exceed 70 nm. On the other hand, the size of real emulsion microcrystals lays in an interval of 50-1000 nm for isometric microcrystals and 300-3000 nm for tabular

microcrystals, that is mostly outside of area of performance of the Rayleigh equation.

Meanwhile there are a number of the approaches allowing to apply a turbidimetric method for research of particles of the large size. For example, Meehans with the co-authors used this method for study of processes of formation of microparticles of a silver halide sol[11]. The detailed research of the phenomenon of a light scattering by silver halide microcrystals in a dry gelatin layer was carried out Pruss with the co-authors[12-15]. However as the literary and calculated data frequently contradicted each other, we had to carry out own research of laws light scattering by silver bromide microcrystals.

Experimental

The emulsions containing AgBr microcrystals of the various sizes and the forms were made by the standard method of control double jet crystallization. A recrystallization in a gel carried out as follows. The emulsions containing microcrystals of the different size were mixed. If necessary the water-gelatin solution was added up to achievement of required AgHal concentration. Then 1 M potassium bromide solution was added to the mix up to achievement of required pBr value; the sample was placed in tight capacities and quickly cooled in water with temperature 10°C for a jellification. The received samples was stored at room temperature 18±1°C. After certain intervals of time the sample of an emulsion was melted at temperature 40°C and required amount of an emulsion was placed in a volumetric flask with warm distilled water (35°C) and fill up to a label. Then the turbidimetric research of the received samples was carried out with a spectrophotometer Shimadzu UV-2100 or photoelectrocolorimeter PEK-56M. As a result of data processing the dependence of a characteristic turbidity of system on length of a light wave were received. This experimental dependence was compared with theoretical, received on the basis of mathematical model described below. On the basis of this comparison the determination a share of conversion of fine microcrystals and current size of large microcrystals in system was carried out.

Experimental results and discussion

Mathematical model of process of a recrystallization. At the first stage we carried out research of laws of a light scattering by real AgBr microcrystals in interesting us an interval of the sizes. For this purpose a series of monodisperse emulsions was made and the dependencies of a characteristic turbidity on the size of a microcrystal for different lengths of waves are received. The experimental results are presented in figure 1.

On the basis of the received dependencies it was possible to carry out theoretical account of change of turbidity during a recrystallization in a gel. Thus we proceeded from the following reasons:

In system there are two types of microcrystals of the different size - large and fine. By definition the size of large

microcrystals during a recrystallization is increased. Thus, as shown by numerous experiments, the size of microcrystals of a fine emulsion does not essentially vary; the only change of their quantity concentration takes place. The increase of weight of large microcrystals in the closed system is equal to a loss of weight of small microcrystals. For simplicity of account we shall consider all emulsions monodisperse and their contribution to a light scattering strictly additive. Let's consider also crystals as correct spheres.
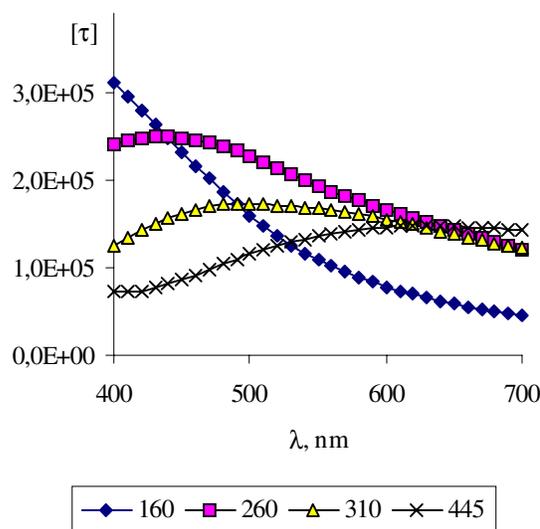

Figure 1. Dependence of the characteristic turbidity on the length of light wave. The digits in legend correspond to the AgBr microcrystals size (nm).

The contribution to a total turbidity of fine microcrystals can be calculated on the Rayleigh equation. But as the size of crystals does not change, it is possible simply to use reference values of a characteristic turbidity and to multiply them on the current AgHal concentration. In turn the current concentration at the given moment of time is equal to initial concentration minus a loss of weight spent for growth of large microcrystals. Let's designate this loss $\Delta[AgHal]$. It is obvious, that thus weight of large microcrystals grows by the same size $\Delta[AgHal]$.

The size of larger microcrystals can be expressed through the given increase. However for this purpose it is necessary to know initial concentration of large microcrystals (l^{-1}). It can be calculated under the formula:

$$N_l = \frac{V(AgHal)_l}{V(MK)_l} = \frac{6 * [AgHal]_l}{\pi d_l^3 * \rho(AgHal)} \quad (1)$$

Where $V(AgHal)_l$ - total AgHal volume in large microcrystals;

$V(MK)_l$ - average volume of one large microcrystal;

$[AgHal]_l$ - concentration of AgHal in large microcrystals (g/l);

d_l - diameter of initial large crystals (cm);

$\rho(AgHal)$ - density of a silver halide (g/cm^3).

The N_l value is a constant, as the amount of large microcrystals during a recrystallization does not vary. Therefore the average diameter of large microcrystals at the any moment of a recrystallization can be calculated under the formula:

$$d_l = \sqrt[3]{\frac{6*([AgHal]_l + \Delta[AgHal])}{\pi * N_l * \rho(AgHal)}} \qquad (2)$$

On known value of an average diameter the contribution to a turbidity of system of large microcrystals can be calculated theoretically through calibration dependencies connecting a specific turbidity to the average size of particles. Thus, it is possible to determine a theoretical turbidity of system for any degree of conversion of fine microcrystals. By comparing theoretic dependence of turbidity with experimental, it is possible to find the current degree of conversion in system and consequently, the average diameter of large microcrystals. For a series of experimental points the dependence of the average size of large microcrystals on time (i.e. kinetic curve) can be received.

Recrystallization of individual monodisperse emulsions. It was experimentally shown that the recrystallization of a monodisperse emulsion containing large AgBr microcrystals does not result in change of its dispersion characteristics. The spectrum of a light scattering for this system remains constant during long time. On the data of the electron microscopic analysis there is a change of a shape of crystals from cubic to octahedral, however their size thus does not vary[5].

It was earlier shown that as a result of a recrystallization of a fine emulsion in a gel could be formed, depending on concentration of microcrystals, either tabular crystals, or mix of tabular and isometric crystals. The theoretical account of change of turbidity in the given system is complicated, as the exact amount of nuclei (centers of growth) is not known. It is necessary to note that for a usual fine emulsion it is usually not too great. The accounts show that linear dependence of turbidity on a share of conversion of microcrystals of a fine emulsion (even on the initial stage of a recrystallization) in this case is observed. Therefore as kinetic curve it is possible to use dependencies of turbidity on time for chosen length of a wave. In figure 2 the similar dependencies for a number of systems with various AgBr concentration are presented. It is possible to see that the speed of process of a recrystallization depends on concentration of microcrystals in system. The change of speed of a recrystallization is in good conformity with change of distance between microcrystals.

A series of experiments with a variation of concentration of an excess potassium bromide in system was carried out also. The results are presented on figure 4. In this case change of speed of a recrystallization is in good conformity with change of solubility of a silver bromide.

Recrystallization of mixes of microcrystals with the large distinction on the size. In this case because of essential difference in solubility during a recrystallization there is a growth of large microcrystals and dissolution fine ones.

The theoretical account is facilitated by the circumstance that the concentration of large crystals in system is constant.

We carried out research of a recrystallization in system containing microcrystals of a fine emulsion and also larger microcrystals of a cubic and octahedral habit. In figure 5 the comparative data on change of the size of large microcrystals during a recrystallization for cases of the different initial size of these crystals are presented. It is possible to see that the speed of a recrystallization is proportional to distinction in a size of microcrystals of a fine emulsion and large crystals.
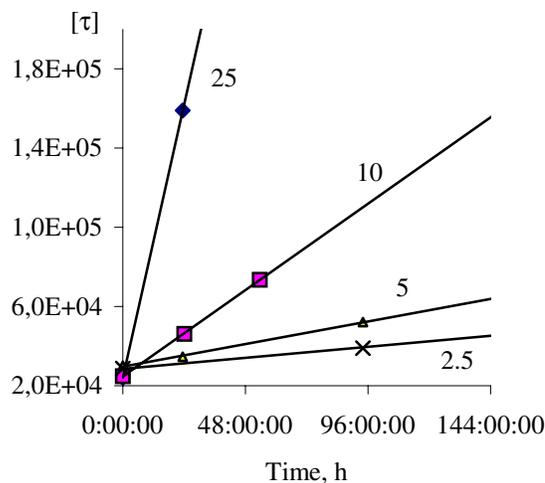

Figure 2. The initial parts of experimental dependencies of characteristic turbidity (λ=490 nm) on the time of recrystallization. The line labels correspond to a silver concentration in system (g/l).
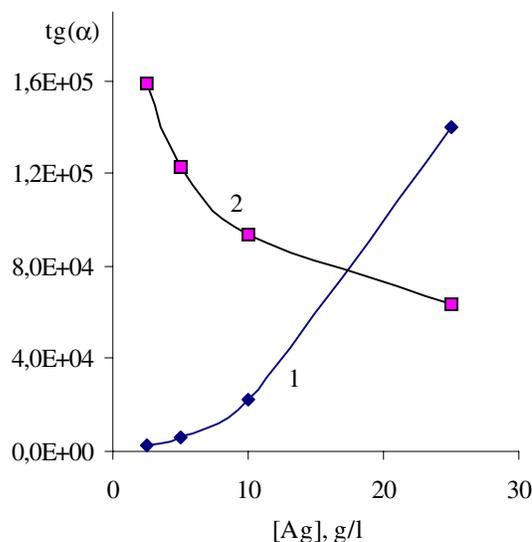

Figure 3. Dependencies of the slope ratio of kinetic lines (1) and interparticle distance (nm$\times$300) (2) on the silver concentration in system.

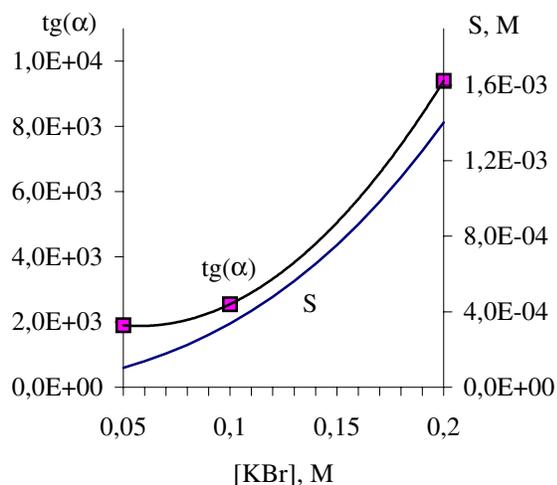*Figure 4. Dependencies of the slope ratio of kinetic lines (tg(α)) and the solubility of silver bromide (mol/l) on the KBr concentration in system.*

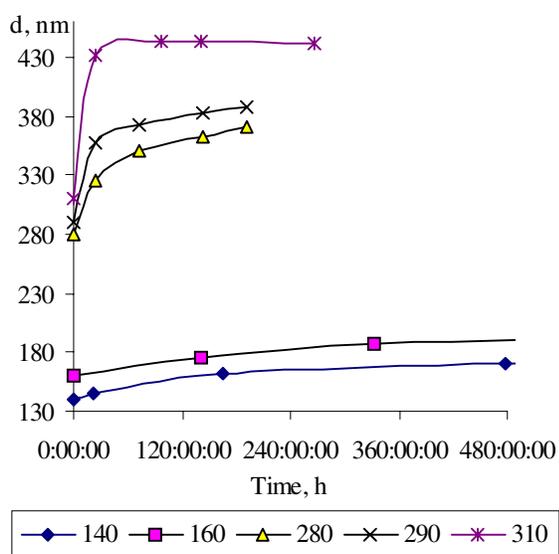*Figure 5. The change of large crystal size during recrystallization. The mass ratio of large and fine crystals is 1:2; pBr=1.0; the total silver concentration in system - 1.7 g/l; size of fine crystals - 65 nm. The digits in legend correspond to initial large crystal size (nm).*

The dependence of the size on time at the large distinction in the sizes between interacting crystals can conditionally be broken on 2 stages (see Figure 6). At the first stage of fast growth rate of large crystals depends on concentration of fine microcrystals (is inverse proportional to distance between small microcrystals), and at the second stage the more slow growth not depends on distance between microcrystals, and proportional only to distinction in size of large and fine crystals. In turn the distinction in size of large and

small microcrystals also renders essential influence on speed of a recrystallization. This situation is illustrated on figure 7. As well as it was necessary to expect, at decrease of size distinction (solubility distinction) the speed of recrystallization process is reduced too.
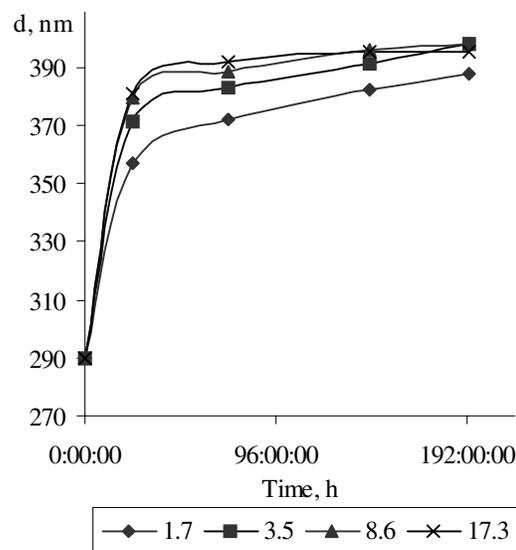

Figure 6. The change of large crystals size during recrystallization. The mass ratio of large and fine crystals is 1:2; pBr=1.0; the initial size of large crystals - 290 nm; size of fine crystals - 65 nm. The digits in legend correspond to total concentration of silver in system (g/l).
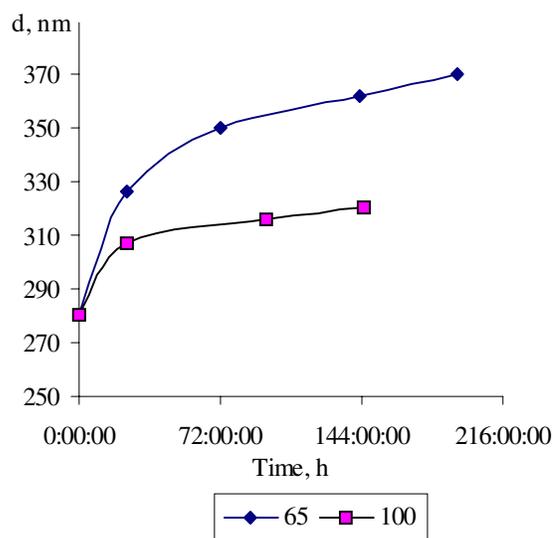

Figure 7. The change of large crystal size during recrystallization. The mass ratio of large and fine crystals is 1:2; pBr=1.0; the total silver concentration in system - 1.7 g/l; initial size of large crystals - 280 nm. The digits in legend correspond to fine crystals size (nm).

It is possible to explain presence of two stages by probable morphological changes occurring to large crystals. At the first stage the growth rate of large crystals more probable is limited by a diffusion of components of the dissolved substance, and, hence, depends on ways of a diffusion. This process proceeds while as a result of growth the surface of large crystals will be replaced from (100) to (111). After that the growth rate of large crystals is limited already by surface reaction and becomes independent from distance between interacting crystals. The increase of weight of crystals appropriate to similar transition depends on a relative ratio of surfaces (100) and (111) at an initial crystal. In other words, it depends on amount of a silver halide necessary for transformation of a primary cubic crystal in a correct octahedron. For the large cubic microcrystals a ratio of surfaces (100):(111) is great, therefore distinction between the first and second stage of growth is clearly expressed. On the contrary for cubes of the small size this ratio is close to one, therefore in this case kinetics of growth of cubic (140 nm) and octahedral (160 nm) crystals practically are identical (see figure 5).

Summing up it is possible to emphasize that the method of a recrystallization in a gel has very rich opportunities on research of the mechanism of growth of AgHal microcrystals of the various forms, size and shape at the different conditions. The further research in with this area could help to understand many till now not clear details of process of a mass crystallization.

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