

# A Comparison Between Calculated and Experimentally Estimated Tabular Grain Growth Rate Constants

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## Introduction

Silver halide tabular grains are widely applied for photographic films preparation. Nowadays two principally different points of view on the tabular grain formation and growth mechanism exist - diffusion and coalescence ones<sup>1,2</sup>. Uncertainty about the real mechanism of the formation and growth is preclusion for the optimisation of multiple precipitation conditions and hence improvement of the tabular grains monodispersity. Formation of the tabular grains during fine AgHal ripening flows to obtain a reliable information about the tabular grain formation and growth. This process can be used as a model of the early stage of the tabular grain precipitation-their formations<sup>3</sup>. Presented paper is dedicated to the study of the tabular AgBr grain growth kinetics of fine AgBr ripening.

## Experimental

Precipitated by the double jet technique fine AgBr has average size of 0,07  $\mu\text{m}$ , Cv not higher than 15% and cubic shape. Then the fixed volume of the fine emulsion was put into a bulb and the toughly closed bulb was shaken until all fine grains transformed into the tabular grains. A concentration of the fine grains was measured in probes sampled at regular intervals by means of nephelometric technique.

The growing tabular grain size, thickness, variation coefficient and tubularity were traced by means of electron and optic microscopy. Fine grain size was measured with disk centrifuge.

## Results and Discussion

Fig. 1 shows electron microphotography of emulsion samples picked during fine AgBr ripening. It is seen that the number of the fine grains decreases with the enlargement of the tabular grains. The fine grain size therewith doesn't change. Fig.2 shows the kinetics of the tabular grain growth. Under the whole range of the experiment conditions it kept an S-shape. Conditions of the growth kinetic measurements are followed in table I.

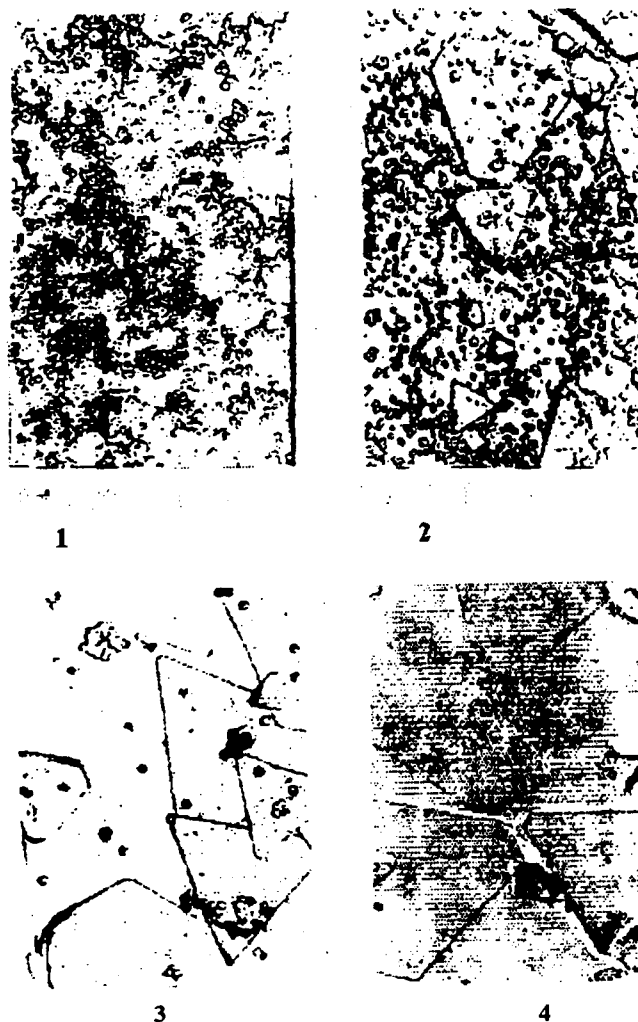


Figure 1. Electron photographs of the coal replies of the ripening fine emulsion. A - 0 min; B - 15 min; C - 45 min; D- 90 min.

Table 1  
Conditions of fine AgBr ripening

Temperature, C	45	50	55	58	60	
KNO <sub>3</sub> conc., M	0	0,1	0,75	1	1,5	2
Gelatine conc., %	2	5	6	8		
pBr level	0,7	1	1,5	2	2,5	

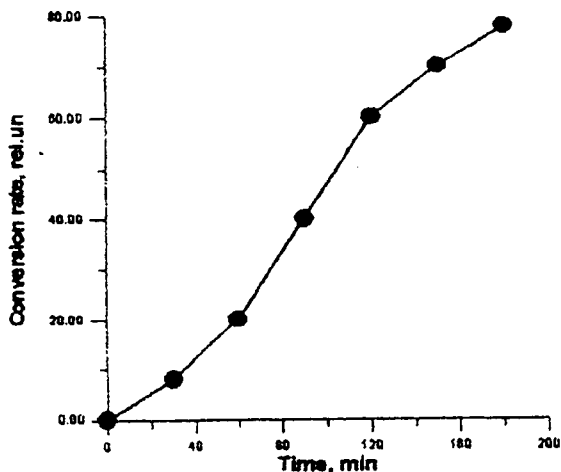


Figure 2 Tabular grain growth kinetics.

The growth rate constant has been got by the Smoluchowski's equation<sup>4</sup>

$$Nt = \frac{N_0}{(1 + t/T)^2} \quad (1)$$

Here T is the half-time of coagulation. At the moment when current time t is equal to the half-time of coagulation T the ratio between the initial fine phase density and current phase density is  $N_0/Nt = 4$ .

It is shown that the growth rate constant depends on the fine phase density. It means that obtained constant values are pseudoconstant. Since the Smoluchowski's constant is a complex unit (see eq.2) it is plausible to account an influence of the experiment conditions on it.

$$K = \frac{RT \exp(-F\zeta / RT)}{Na\eta} \quad (2)$$

As it follows from eq.2 a viscosity of the emulsion  $\eta$  must influence an aggregation rate constant. The emulsion viscosity depends on the solid phase density and can be taken into account using the Einstein equation:

$$h = h_0(1 + \alpha\phi) \quad (3)$$

here h is a current viscosity,  $h_0$  is a gelatine solution viscosity,  $\alpha$  is particle shape factor equal for cubes to 2,5 and  $\phi$  is solid phase space density. The experimentally obtained constant conversion with respect to the emulsion viscosity gives in all cases a constant value of  $2,8 - 2,9 \cdot 10^{-16} \text{ l}^{-1}\text{sec}^{-1}$ . This result allowed us to compare constant value obtained in different conditions of the experiment.

### Gelatine Concentration

It is seen on fig.3 that the constant value doesn't change up to the gelatine concentration 3% and at the concentration higher than 3% it decreases drastically. When the gelatine

concentration is higher than 5% it is stable again. Such a drastic constant value decrease can be explained by formation of the "structural - barrier" which precludes particles approaching and thus decreases a coalescence rate. Similar effects are reported elsewhere. Antoniadis and Way<sup>5</sup> have shown that the DLVO theory isn't observed obeyed at gelatine/silver ratio (Rgs) less than 50 g/mol. A conversion of this Rgs value to the emulsion grain surface gave a value of  $8 \text{ mg/m}^2$ , which corresponds to the gelatine adsorption monolayer. Herz and Helling<sup>6</sup> have measured to the threshold Rgs value as  $3 \text{ mg/m}^2$ . Unfortunately due to the difference in experiment conditions it is difficult to compare the threshold Rgs value in our experiments ( $23 \text{ mg/m}^2$ ) with those reported elsewhere. Anyway it is explicit that the gelatine influence on the tabular grain growth corresponds to the coalescent mechanism.

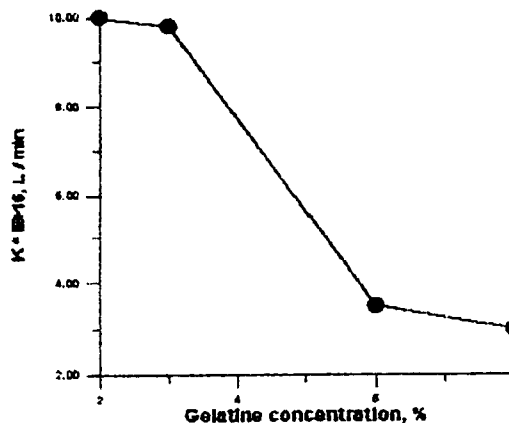


Figure 3. Growth rate constant dependence on gelatine concentration

### Temperature

A dependence of the growth rate constant on the temperature and unrelated salt concentration is shown on fig 4.

It is seen that constant in the equation (2) is a pseudoconstant. An elimination of the temperature has been carried out in order to take into account its influence on the constant and to get its true value. The temperature influences the rate constant by both the diffusion factor (D) and the electrostatic stable factor (e). Division of the experimentally obtained rate constant by the temperature allows to eliminate the diffusion factor influence and it results in another oblique line. Though the e factor is an exponent, it is practically linear in a temperature range of the experiment. It gives an opportunity to estimate value of the Sterne potential ( $\zeta$ ). The value of the  $\zeta$  potential for which  $K/T$  doesn't depend on T has been calculated by means of iteration method. The calculated value -28 mV stays in a good agreement with data obtained for different emulsions by means of electrophoresis (from -5 up to -40 mV)<sup>7</sup>.

The scaling factor of the AgBr solubility in the temperature range 0 - 60°C is higher then unit thus proving

impossibility of the diffusion mechanism of the tabular grain growth under conditions of our experiment.

### Unrelated Salt Concentration

Any unrelated salt increases ionic strength of the solution and causes a decrease of the  $\zeta$  - potential. Consequently linear increase of the rate constant with the unrelated salt concentration growth is a result of the potential decrease. It gives an opportunity to calculate values of the  $\zeta$  - potential for the whole range of  $KNO_3$  concentration (0 to 2 mol/l) assuming that K is constant. The calculated values stay in a good agreement with data reported in<sup>7</sup> and are enlisted in table 2.

**Table 2 Ionic strength and corresponding values of the  $\zeta$ -potential**

Ionic strength mol.l	0,001	0,7	1	1,5	2
Potential mV	-28	-20,5	-17	-11	-7

A reduction of the  $\zeta$  - potential makes a diffusion layer thinner. That results in the colloid system stability drop down and thus accelerates tabular grain coalescent growth.

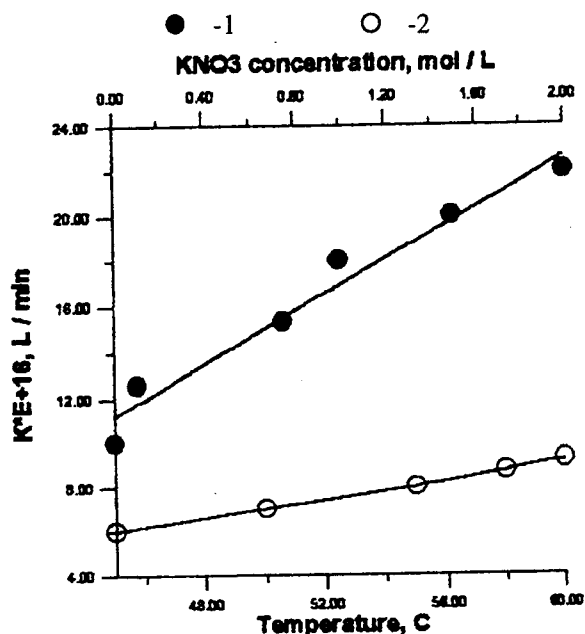


Figure 4. Growth rate constant dependence on  $KNO_3$  (1) concentration and temperature (2).

The increase of the ionic strength increases also  $AgHal$  solubility due to the so called "salt effect" and thus it might make the diffusion growth more distinct. However, a variation of the solubility calculated as a function of the ionic strength reveals a non-linear character and it proves that the whole process proceeds through the coalescence.

### pBr Level

Fig.5 shows K variation with an equilibrium bromide ion concentration. Bromide ion adsorption is nearly constant in the pBr range under investigation. It means that neither the  $\zeta$ - potential nor electrostatic attraction between a regular fine grain and a side face of growing tabular grain change noticeably. The solubility of  $AgBr$  increases in a magnitude of one order in the pBr level under investigation but it doesn't change the shape of the growth kinetics. One can suppose that the increase of the  $AgBr$  solubility can accelerate the coalescent growth by a diminution of the regular fine  $AgBr$ . Since the coalescent growth constant of a bimodal system is proportional to the difference of phase diffusion factors it must increase with the regular fine  $AgBr$  diminution. Above mentioned results prove that in absence of silver halide solvents the conversion of fine  $AgBr$  in tabular grain proceeds through the coalescence and the diffusion contribution to the growth is negligible.

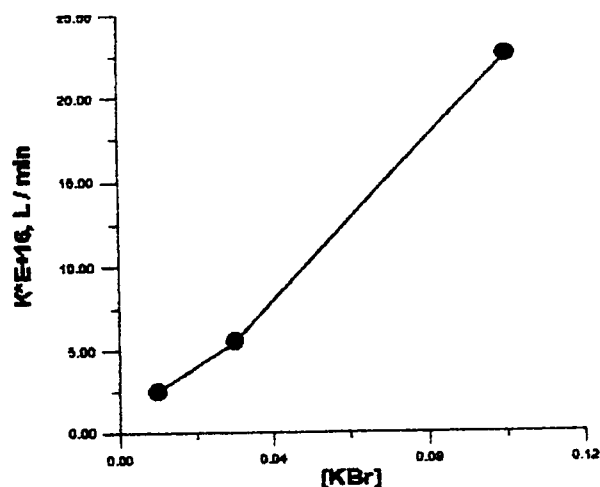


Figure 5. Growth rate constant dependence on excessive bromide ion concentration.

### Conclusions

Quantitative estimations of tabular grain growth during ripening of fine  $AgBr$  prove a coalescent nature of this process. Estimated from the measured data as the Smoluchowski's equation constant values of the growth rate constant stay in very good agreement with some other relevant data.

### References

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