X-Ray Diffraction Analysis of Differently Prepared AgI. III.

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The influence of the concentration of the constituent and coagulating ions, surface active agents, pH, and the rate of precipitation on the cubic/hexagonal ratio of AgI and on the size of AgI crystallites formed *in statu nascendi* sols has been studied. In the concentration regions $c_{KI} = 1.0 \times 10^{-5}$ *M* to 1.00 *M* and $c_{AgNO_3} = 1.0 \times 10^{-6}$ *M* to 2.00 *M* different amounts of cubic and hexagonal AgI were obtained. The pure hexagonal modification was found only at 1.00 *M* KI. At *p*I 4 22% of cubic AgI was obtained. From aqueous solutions containing AgNO₃ (1×10^{-6} to 2.00 *M*) no pure cubic AgI can be obtained. At *p*Ag 1—2 the maximum amount (80%) of cubic AgI was formed. The aging process does not change the cubic/hexagonal ratio but influences the growth of crystallites. The rate at which the precipitation components are mixed influences the dispersity and the cubic/hexagonal ratio, which on the other hand also depend on the concentration of univalent and bivalent coagulating ions. The acidity of the system (pH = 0.1 — 5.8) does not significantly influence the dispersity and the cubic/hexagonal ratio of AgI. Surface active agents (SAA) in the concentration region from 1.0×10^{-7} *M* to 1.0×10^{-4} *M* do not influence the crystal structure; they influence, however, the dispersity of the particles of sols hindering their growth. By dilution of the complex solution of AgI — KI with water AgI sols were formed. At lower initial concentration of KI the percentage of hexagonal AgI was higher. In sols formed by dilution of the complex solution of AgI — AgNO₃ with water, more cubic AgI was found at lower initial concentration of AgNO₃. By cooling a hot complex solution of AgI — KI (2.0 *M* KI) from 160° C to room temperature (0.2° C/min) 100% of cubic, transparent AgI crystals were formed.

INTRODUCTION

Silver iodide is known to exist at room temperature and at normal atmospheric pressure in aqueous media in two crystallographic modifications: the cubic α sphalerite type, and the hexagonal β wurtzite type[1-5]. At extremely high pressure and/or temperature AgI is found to exist in several other modifications[6]. Consequently, during precipitation and subsequent aging of AgI usually mixtures of two modifications are obtained[3,7] in the supernatant liquor. It is also known that during aging the crystallites of AgI sols and suspensions are usually getting coarser *via* Ostwalds ripening[7,8]. Experiments demonstrated that the heterogeneous exchange of AgI—I⁻ and AgI—Ag⁺ continues for hours, weeks or even months after precipitation, *i. e.* during

the aging periods[9]. It has been shown that the exchange of I⁻ ions, until the equilibrium is established, is caused by recrystallization of AgI. The ion exchange of Ag⁺ is caused by recrystallization of AgI and by diffusion of Ag⁺ into the solid during the early stages. The diffusion, however, takes place also after recrystallization equilibrium has been established. This is obviously due to extremely high differences in the diffusion coefficients between I⁻ and Ag⁺ ions[4]. Under given conditions, during the first period after precipitation, coagulation, i. e. aggregation of small primary crystallites into agglomerates can also take place. It has been shown that in a solution containing an excess of I⁻ ions precipitates of the hexagonal modification are predominantly formed, whereas in the supernatant liquor containing an excess of Ag⁺ ions precipitates of cubic modification are predominantly found[1,4,5,7].

These general observations suggest that there is a complex interdependence between the mentioned processes. A systematic experimental study could contribute towards our understanding of the double layer processes by which the precipitation, colloid stability and coagulation and the aging processes are governed. Therefore, the influence of precipitation conditions upon the ratio of crystallographic modifications, upon the role of modification in colloid stability and coagulation, and upon the conditions of transition from one modification to another will be systematically investigated.

In this paper a systematic X-ray diffraction analysis of differently prepared AgI is described. Quantitative data on the cubic/hexagonal ratio, on the primary particles and the size of AgI crystallites in suspensions in dependence on a series of parameters defining the precipitation and aging conditions are given.

EXPERIMENTAL

Preparation of Systems

All systems were prepared by mixing equal volumes of the solutions of precipitating reagents. Depending on the system, mixing was carried out in one of the following ways:

a) AgNO₃ solution was added to a mixture of KI + coagulation electrolyte;

b) A mixture of AgNO₃ + coagulation electrolyte was added to the KI solution;

c) KI solution was added to the mixture of AgNO₃ + coagulation or stabilization electrolyte;

d) A solution prepared by mixing KI solution with the coagulating or stabilizing electrolyte solution was added to the AgNO₃ solution.

Initial concentrations of the AgNO₃ and KI solutions were in the range of 1.25×10^{-4} M to 4.00 M. After mixing an excess of KI and/or AgNO₃ remained in the colloid system. The corresponding pI and/or pAg values are given in the figures. All the systems were prepared to contain about 100 mg of AgI, the quantity necessary for the X-ray analysis.

In order to investigate the influence of the rate at which the reaction components are mixed the precipitation systems were prepared by continuous addition of KI solution to AgNO₃ solution and AgNO₃ solution to KI solution, respectively. The solution to be added (1000 ml 0.0020 M KI to 500 ml 0.80 M KNO₃ + 500 ml 0.0080 M AgNO₃ and/or 1000 ml. 0.0020 M AgNO₃ to 500 ml 0.80 M KNO₃ + 500 ml 0.0080 M KI) was stirred with a magnetic stirrer. The times of addition were t_p = 10, 100, 1000 minutes, and time of aging t_G = 10, 100, 1000 minutes.

With the aid of a NETSCH Model 406 temperature programmer AgI (0.05825 g, 0.11665 g, 0.23420 g) in 2.00 M KI solution (0.2500 ml) was heated to 160⁰ C in a sealed Pyrex ampulla and then cooled continuously (0.2⁰ C/min) to 20⁰ C. In this way transparent AgI crystals were obtained.

X-Ray Diffraction Analysis

The proportions of cubic and hexagonal modifications in AgI samples were determined using a Philips diffractometer with a scintillation counter and a single-channel height pulse analyser. Filtered copper $K\alpha$ radiation was used in all cases.

Hexagonal diffraction line (100) at the Bragg angle $\Theta = 11.2^0$, and overlapping diffraction lines (111) and (002) at $\Theta = 11.9^0$ of the cubic and hexagonal modification, respectively, were recorded. Sometimes we also used hexagonal line (101) at $\Theta = 12.7^0$. The square of the structure factor values of these lines are:

$$F^2_{(100)} = f^2_{Ag} + 2 f_{Ag} f_I + f^2_I$$

$$F^2_{(111)} = 16 f^2_{Ag} + 16 f^2_I$$

$$F^2_{(002)} = 4 f^2_{Ag} + 4 f^2_I$$

$$F^2_{(101)} = 3 f^2_{Ag} + 3 f^2_I - 3 \sqrt{2} f_{Ag} f_I$$

where f_{Ag} and f_I are atomic scattering factors for Ag and I.

Taking into account other factors affecting the diffraction intensities (the polarization factor, the Lorentz factor, the geometrical factor, the multiplicity factor, and the number of atoms in the unit cell)[10] we got the following relations between the integrated diffraction intensities:

$$I_{(111)} : I_{(100)} : I_{(101)} : I_{(002)} = 4 : 1.72 : 1.13 : 1$$

Thus the ratio of the proportions of cubic and hexagonal modification is

$$K/H = \{[I_{(111) + (002)} - (I_{(100)}/1.72)]/4\}/[I_{(100)}/1.72]$$

where $I_{(111) + (002)}$ and $I_{(100)}$ are observed intensities of lines at $\Theta = 11.9^0$ and $\Theta = 11.2^0$ respectively. A series of independent experiments were run with each sample and it was found that the preferred orientation of the crystallites could be neglected, because the fluctuations of the results were less than 2%. This conclusion was confirmed by using the overlapping diffraction lines (220) and (110) at $\Theta = 19.6^0$ of cubic and hexagonal structure respectively.

The crystallite size was evaluated according to Scherrer's formulae[11].

$$R = \lambda [\beta_i \cos \Theta]^{-1} \qquad\qquad R = 0.9 \lambda [\beta_{1/2} \cos \Theta]^{-1}$$

using the integral breadths, β_i, and half-maximum breadths, $\beta_{1/2}$, respectively (λ is the wavelength). In order to estimate the instrumental broadening of diffraction lines, we used the (111) reflection of high purity germanium powder at $\Theta = 13.65^0$ with no lattice distortion and no crystallite size broadening. The pure diffraction breadths were deduced by the use of Alexander's correction curves[11]. The accuracy of the determination of the absolute crystallite size is reduced with a decrease of pure diffraction broadening. If the crystallites are larger than about 1000 Å the relative rather than the absolute changes of the crystallite size from sample to sample are to be considered.

During recording of the X-ray diffraction patterns all AgI suspensions were in contact with the original supernatant liquor.

RESULTS

Crystallographic characteristics and size of AgI crystallites depend on the excess of I^- and Ag^+ in the system (Figs. 1 and 2). In systems with an excess of 1.0 M KI AgI appears in the pure hexagonal modification ($K = 0\%$ of cubic AgI). At higher pI values the percentage of cubic modification increases, reaching its maximum (80%) at pI 4, at pI 5 the K value decreases.
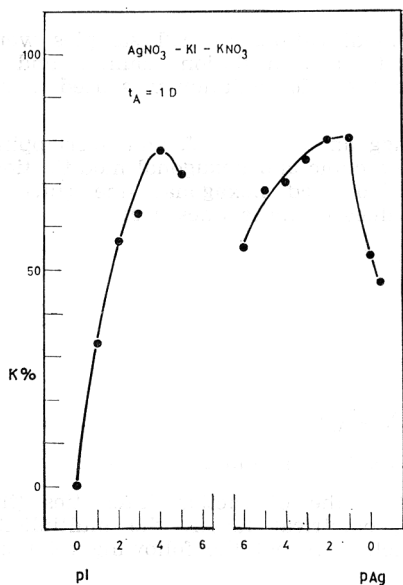
Fig. 1. Percentage of cubic AgI (K %)
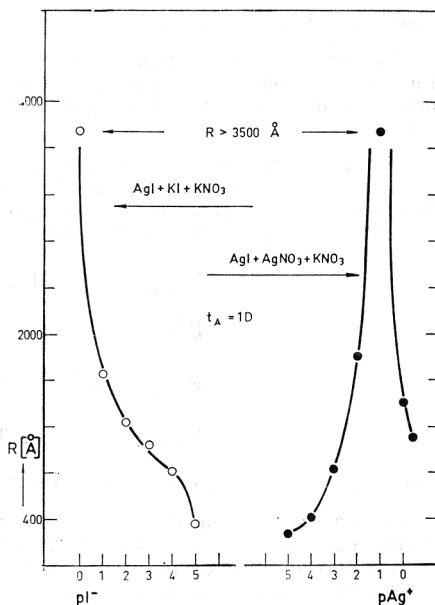plotted against pI and pAg. Aging time
$t_A = 1$ day, $\alpha = 1.0$.

Fig. 2. Size of AgI crystallites R (Å)
plotted against pI and pAg. Aging time
$t_A = 1$ day, $\alpha = 1.0$.

At pAg 6 (the isoelectric point) the K value is 54%, however with a decrease of pAg to 1 the K value increases to 82%. At pAg 0, K = 48%. At pI 0 and pAg 1 the AgI crystallites are the largest (Fig. 2). By aging from 1 to 30 days the AgI crystallites are getting larger (Figs. 3, 4 and 5) whereas the K value remains unchanged. At higher KI and $AgNO_3$ concentrations the crystallite growth is faster.

With the increase in the concentration of KNO_3 (the coagulating electrolyte) from 0.10 to 1.00 *M* the size of AgI crystallites decreases (Tables I and II), however it increases with the increase in the concentration of K_2SO_4 from 0.00020 to 0.20 *M* (Table II). At the concentrations of 1.00 *M* KNO_3 and 0.20 *M* K_2SO_4 the percentage of cubic AgI increases. The acidity of the system was not found to be a very important parameter (Table III). At pH 0.11 the crystallite size was 630 Å and it increased to 820—850 Å at pH 2.20—5.83, while the crystallographic modification did not depend on pH.

The amount of AgI formed per liter of the sol (at pAg 3 and pI 3) plays an important role in the dispersity and crystallographic modification of AgI at pI 3 (Table IV). At pI 3 the crystallite size and the K value increase with an increase in the amount of AgI. At pAg 3 the K value remains constant while in the presence of a larger amount of AgI the crystallite size increases.

The concentration and chemical nature of the surface active agents (SAA) such as *n*-myristylamine nitrate, K-*n*-myristinate and TRITON X-305 (Table V) do not change considerably the crystallographic properties of AgI sols in the concentration region from 1.0×10^{-7} *M* to 4.0×10^{-4} *M*. In this region the crystallite size is inversely proportional to the concentration of the SAA.
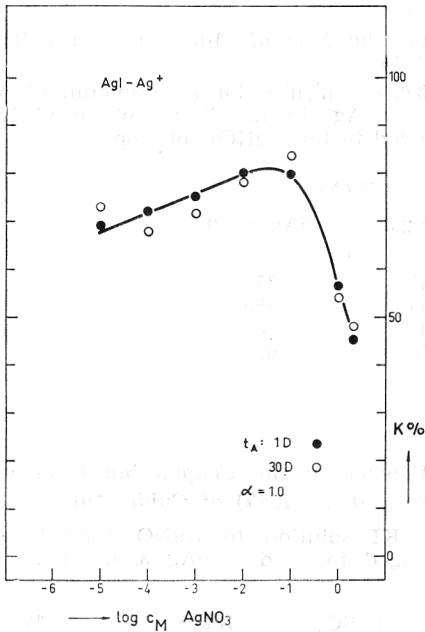
Fig. 3. Percentage of cubic AgI (K%) for different aging times ($t_A = 1$ and 30 days) plotted against the logarithm of concentration of $AgNO_3$.
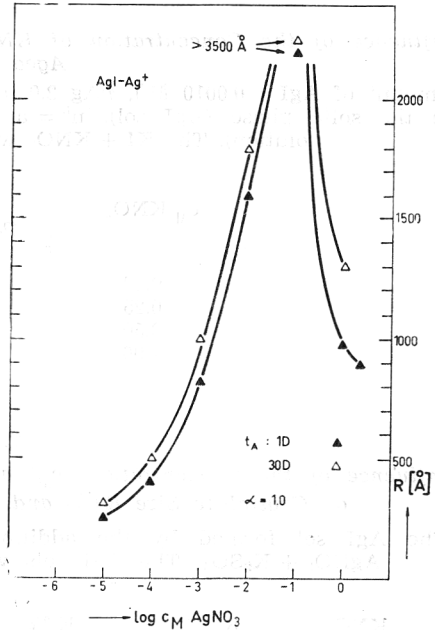
Fig. 4. Size of AgI crystallites R (A) plotted against pAg. Aging times $t_A = 1$ and 30 days.

The rate at which the reaction components are mixed as well as the age of the sols are important parameters for both the crystallographic modification (Fig. 6, pAg 3) and dispersity (Figs. 6, 7, pAg 3, pI 3). In slowly precipitated systems ($t_p = 1000$ min) containing an excess of $AgNO_3$ (pAg 3)
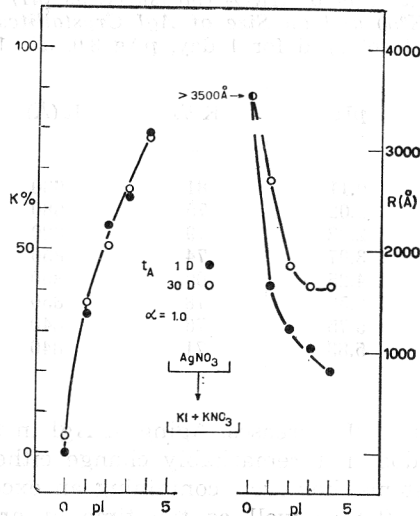

Fig. 5. Percentage of cubic AgI (K%) and crystallite size R(A) plotted against pI.

TABLE I

Influence of the Concentration of KNO_3 on the Size of AgI Crystallites $R\,(\text{Å})$
Aged for 1 Day

Amount of AgI = 0.0010 M/l, pAg 2.0, pAg 3.0. $\alpha = n^s/n^L = 1.0$. n^s = amount of Ag^+ in the solid phase (AgI sol). n^L = amount of Ag^+ in the liquid phase ($AgNO_3$ solution). The KI + KNO_3 was added to the $AgNO_3$ solution.

$c_M\ KNO_3$	R (Å)	
	pAg = 2.0	pAg = 3.0
0.10	2030	950
0.25	1500	850
0.50	1000	780
1.00	620	660

TABLE II

Influence of the Concentration (c_M) and Valency of the Coagulating Electrolyte
on Crystallite Size $R\,(\text{Å})$ and on Percentage ($K\,\%$) of Cubic AgI

The AgI sol formed by the addition of KI solution to $AgNO_3$ + KNO_3 and $AgNO_3$ + K_2SO_4. The AgI sols were aged for 1 day, pAg 3, $\alpha = 1.0$.

$c_M\ KNO_3$	R (Å)	K %	$c_M\ K_2SO_4$	R (Å)	K %
0.10	900	75	0.00020	400	69
0.25	850	81	0.0020	540	77
0.50	780	86	0.020	680	84
1.00	620	89	0.20	900	88

TABLE III

Influence of the Concentration of HNO_3 (measured as pH) on Percentage of Cubic
AgI ($K\,\%$) and on Size of AgI Crystallites $R\,(\text{Å})$
AgI sol aged for 1 day, pAg 3.0, $\alpha = 1.0$.

pH	K %	R (Å)
0.11	81	630
1.02	75	680
2.02	79	820
3.07	74	850
4.25	69	850
5.50	78	850
5.75	76	840
5.83	71	840

the percentage of cubic AgI increases. Aging of AgI in the solution containing an excess of $AgNO_3$ does not remarkably change either the K value or the crystallite size. In systems, however, containing an excess of I⁻ (Fig. 7, pI 3), the precipitation rate (t_p) as well as the time of growth (t_A) of the AgI particles change remarkably the crystallite size. The influence of aging time

TABLE IV

Influence of the Amount of AgI (n^S) on Crystallite Size $R(\mathring{A})$ and on Percentage of Cubic AgI

pAg 3.0 $(n^L = 0.0010\ M/l\ AgNO_3)$ and pI 3.0 $(n^L = 0.0010\ M/l\ KI)$

α	0.10	1.00	10.0	
K %	76	79	78	
R (Å)	520	720	2050	pAg = 3.0
K %	55	63	72	
R (Å)	650	1150	1150	pI = 3.0

(t_G) (defined as the time of growth in the supernatant liquor after flocculation) on crystallite size is considerable in systems obtained by a high rate precipitation ($t_p = 10$ min).

The crystallite size and the percentage of cubic AgI increases with increasing initial concentration of KI and decreasing initial concentration of $AgNO_3$.
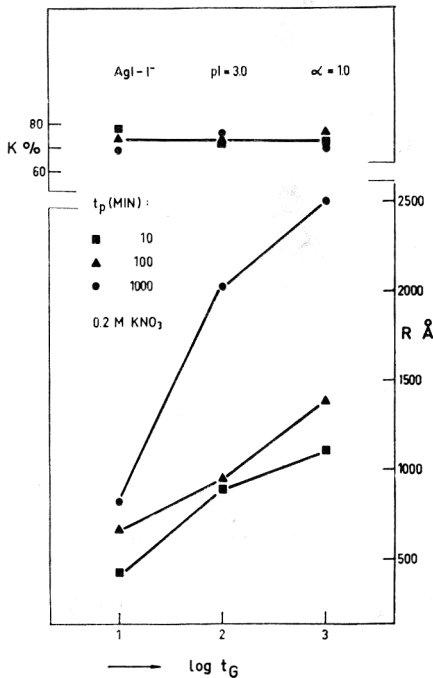

Fig. 6. Percentage of cubic AgI (K %) and crystallite size R (Å) plotted against aging time (t_G = 10, 100, 1000 minutes) in supernatant liquor. Precipitation rates t_p = 10, 100 and 1000 min, pAg 3.
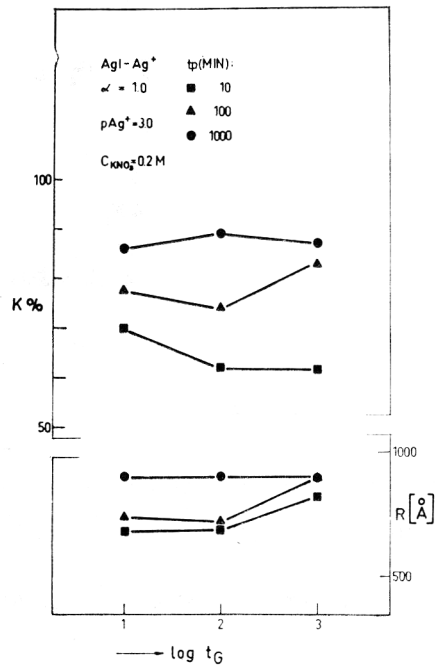
Fig. 7. Percentage of cubic AgI (K %) and crystallite size R (Å) plotted against aging time (t_G = 10, 100, 1000 minutes) in supernatant liquor, pI 3. Precipitation rates t_p = 10, 100 and 1000 min.

TABLE V
Influence of Concentration (c_M SAA) on Size of AgI Crystallites R (Å)
SAA = n-myristylamine nitrate (MAH)NO$_3$, K-myristinate (K—M), TRITON X-305
(T-X-305), and Rhodamine 6 G (R—6 G). Aging time of AgI; 1 day pAg 3, $\alpha = 1.0$.

c_M SAA	R_{AgI} (Å)			
	(MAH)NO$_3$	K-M	T-X-305	R-6 G
1.0×10^{-7}	420	540	560	580
1.0×10^{-6}	380	580	580	480
1.0×10^{-5}	340	580	580	350
4.0×10^{-4}	340	380	520	200

Clear, transparent AgI crystals were formed by cooling the hot complex solution of AgI — KI to room temperature (Fig. 8). The percentage of the hexagonal modification of AgI crystals aged 1 day prior to X-ray diffraction analysis was 0% and after four years it remained unchanged. The size of the AgI crystallites is larger at higher concentrations of KI and when small amounts of AgI are present.
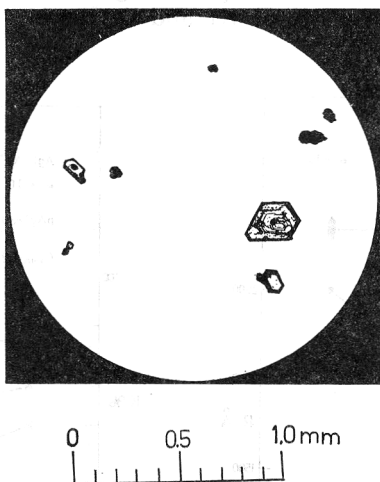

Fig. 8. AgI crystals formed by cooling the complex solution of KI — AgI.

TABLE VI
The Formation of AgI by Water Dilution of Complex Solutions of AgI—KI and AgI—AgNO$_3$ to 0.1 M KI and/or 0.1 M AgNO$_3$
Initial concentration (c_M) of KI and AgNO$_3$ = 1.0, 2.0, 3.0, and 4.0 M, $t_A = 1$ day.

c_M KI	K %	R (Å)	c_M AgNO$_3$	K %	R (Å)
1.0	30	2000	1.0	84	2000
2.0	39	2450	2.0	69	1000
3.0	49	2130	3.0	66	1380
4.0	54	2730	4.0	49	1630

DISCUSSION

The aim of our work was to find out to what extent (*i*) the concentration of constituent I⁻ and Ag⁺ ions (*ii*) the mode of preparation of the systems and (*iii*) the concentration and chemical nature of the coagulating agents influence the ratio between the hexagonal β and cubic α modifications and the size of AgI particles in silver iodide sols.

There are many very interesting papers which discuss crystallographic polymorphism of AgI. Bassett and Takahashi[12], investigating polymorphism of AgI, concluded that β-hexagonal AgI is stable at low temperature and low pressure. Bloch and Möller[1] found that α-cubic AgI is formed in systems containing an excess of silver ions or by crushing cold melted AgI, while β-AgI is formed in systems containing an excess of iodide ions or by slow cooling of melted AgI. An equivalent mixture of α and β AgI is formed by equivalent precipitation. The K value of 55 ± 3⁰/₀ for cubic AgI found in the isoelectric AgI precipitate is in accordance with these results[7]. Burley established that the mixture of α and β AgI exists in the temperature range from — 272⁰ C to + 147⁰ C[2]. On the basis of very precise X-ray analysis Chateau, Cugnac, Moncet, and Pouradier[13] concluded that the preparation conditions of AgI have no influence on the unit cell parameters of β-AgI. Chatterjee[14] found that the crystallite size is about 50 mμ and that it increases by aging, while the crystallographic modifications do not change. Cohen and Dobbenburgh[3] always obtained mixtures of α and β-AgI in differently prepared AgI. Jordan and Pochon[4] distinguish three madifications of AgI: cool cubic α-AgI, β-hexagonal AgI and hot cubic γ-AgI (stable over 146.6⁰ C). Using a radioactive tracer technique they determined very precisely diffusion coefficients of Ag⁺ and I⁻ ions in various crystallographic modifications of AgI. Sieg[15] concluded that by increasing the vapour pressure of elementary iodine over AgI, α-AgI is changed to β-AgI and *vice versa*. Yamada[5] found that α-AgI if formed in systems containing an excess of silver ions and divalent anions, whereas β-AgI is formed in systems with an excess of iodide ions and divalent cations. R. H. Ottewill *et al.*[17] showed that α and β AgI are formed in the presence of dodecylpyridinium iodide (DPyI). On the basis of electron-microscopy data they suggested that small quantities of DPyI influence the nucleation process and that DPyI ions are probably partly adsorbed on primary AgI particles causing a decrease of the charge and thus facilitating the crystal growth.

Deaton, Davis, and Adams[6] investigating polymorphism of AgI at high pressure concluded that AgI exists also in pseudotetragonal and tetragonal forms.

Some authors[1,5,14,15] reported that the hexagonal structure was found in systems containing an excess of iodide ions or iodine vapour. According to our results the percentage of the hexagonal modification is highest at high concentration of free KI in the solution after AgI has been formed. In systems containing an excess of KI the maximum of the curve (**Fig. 1**) corresponds to the one of the »tyndallometric value — pI« curve[8]. When the concentration of free AgNO₃ is increased the picture is not so simple and an excess of Ag⁺ in the system does not necessarily mean that pure cubic AgI is present. In the mixture of α and β-AgI which is formed in the system at pAg 6 the cubic modification prevails[1,7]. The point on the »K⁰/₀—pAg« curve denoting the smallest percentage of cubic AgI at pAg 6 corresponds to the

isoelectric point of the AgI sol. The greatest amount of cubic crystallites is found at the maximum (»K⁰/₀—pAg« curve) which divides the positive limit of complex solubility[8]. By increasing the concentration of $AgNO_3$ in the liquid phase AgI is complexly dissolved and the percentage of cubic modification decreases. If free iodine either in the form of I^- or I^0 [1,5,14,15] is the agent that determines the formation of hexagonal modification, it is very likely that free Ag^+ determines the formation of cubic AgI. An increase in the concentration of Ag^+ causes the formation of the complex, associate, quasi complex or complexoid[16] which influences, probably in a way different than does $AgNO_3$, the α/β ratio. Consequently, with an increase (over pAg 1) in the concentration of $AgNO_3$ the amount of cubic AgI decreases (Figs. 1,3). Such an associate, complex or complexoid is unnoticable in the region from pAg 6 to maximum (pAg 1—2)[16] and the influence of the mass of free $AgNO_3$ on the formation of cubic AgI is quite obvious. All this indicates that the concentration of free constituent ions in the system is responsible for the formation of α- and β-modifications of AgI. The »K⁰/₀—pI, pAg« curve is in good agreement with the tyndallogram of AgI, however, the curve denoting the size of the AgI crystallites (at pAg 1—2) is in a much better agreement with the same tyndallogram (Fig. 2). The aging of sols with an excess of $AgNO_3$ and KI, respectively, influences only the growth of the AgI crystallites (Figs. 3, 4, 5) while the α/β ratio remains unchanged, which is in accordance with the results of Chatterjee[14].

The results published so far[1-5,12,15], including our own, show that the dispersity (pAg 3, pI 3, Figs. 6, 7) and the α/β ratio (pAg 3, Fig. 6) are influenced by the rate at which the precipitation components are mixed. The rate of mixing (t_p) in systems containing an excess of Ag^+ has an influence on the α/β ratio, whereas in those with an excess of I^- this influence is weak. At room temperature the hexagonal AgI is more stable[12] than the cubic AgI. This means that by a more rapid precipitation in the system with pAg 3 a greater amount of hexagonal than of cubic AgI is formed regardless of the excess of $AgNO_3$ in the system. Slow precipitation as well as fast precipitation in solutions with an excess of iodide ions (pI 3) result in the formation of the same mixture of α and β AgI. Under such conditions about 70⁰/₀ of cubic AgI is formed (Fig. 7). The results given in Figs. 6 and 7 are not in accordance with those cited by the above authors, excepted some of Yamada's[5] who obtained various compositions of AgI modifications depending on the rate of cooling.

All these results show that the precipitation system $AgNO_3$ — KI is an asymmetric one. The α/β ratio in the AgI sols and the crystallite size do not depend only on the constituent ions and the mode of preparation, but on the concentration and valency of the coagulating ions as well (Table I and II). The results presented in Fig. 2 show that the AgI crystalites are larger at higher concentrations of $AgNO_3$, whereas they are smaller at higher concentrations of the coagulating ions (Table I). This is probably due to the difference in the rate of nucleation and to the growth of crystals.

When comparing the influence of univalent ions with that of divalent ions it can be seen that at higher concentration of the divalent coagulating ions the AgI crystallites are larger (Table II). All the mentioned results are in accordance with the results obtained by Yamada[5] who has found that divalent anions and an excess of Ag^+ have the same effect on the system

(compare the crystallite size for pAg 2 and 3, Table I). The amount of cubic AgI at higher concentrations of univalent or divalent anions, is greater, probably due to faster formation of AgI at higher concentrations of the coagulating ions. When HNO_3 is used as the coagulation electrolyte, the acidity of the system (pH) does not play a significant role. The dispersity and the α/β ratio remained unchanged in the pH region from 2.02 to 5.83 (Table III) while at pH 1 the dispersity was changed (0.1 M NO_3^- corresponds to critical coagulation values for univalent ions). The results presented in Table IV show that at constant concentration of free constituent ions (pAg 3) the α/β ratio does not depend on the amount of AgI. Namely, for $\alpha = 0.1$, 1.0 and 10.0 the K value is approximately 78%. The change of α is considered as the change of pAg. In this case the results obtained for the α/β ratio (Figs. 1, 3) are in good agreement with those obtained for α. Between pI 2 and pI 4 the change of dispersity is much smaller than between pAg 2 and pAg 4 (Fig. 2). The SAA hinder the growth of the AgI crystallites. The SAA do not influence substantially the α/β ratio in the concentration regions in which they coagulate ($10^{-7} - 10^{-6}$ M) and stabilize ($10^{-5} - 10^{-4}$ M) the AgI sols[7]. This is due to the decrease of surface tension on the boundary crystal/electrolyte medium + SAA, in accordance with data of Preston[18].

By cooling a complex solution [AgI—KI—H_2O] from 160° C to 20° C clear, yellowish cubic AgI crystals were formed. This is very interesting, since by precipitation of AgI at room temperature and at high concentration of KI (pI 0) the pure hexagonal modification was obtained (Fig. 1). By precipitation in aqueous solutions at room temperature no pure cubic modification was found. However, from solutions containing a large excess of KI heated above the temperature of phase transformation and then slowly cooled, the pure cubic AgI can be obtained. The cubic modification obtained by cooling probably corresponds to the high temperature cubic modification after Jordan and Pochon[3].

All the results obtained show that the percentage of cubic and hexagonal modifications of AgI depends on the concentration and chemical nature of the electrolytes present in the system.

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IZVOD

Rendgenska difrakciona analiza različito pripremljenog AgI. III.

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Istraživan je utjecaj koncentracije konstitutivnih i koagulacionih iona, tenzida, pH i brzine precipitacije na omjere kubične i heksagonske modifikacije AgI i na veličinu kristalita u *in statu nascendi* formiranim solovima AgI. U koncentraciji od $c_{KI} = 1.0 \times 10^{-5}$ M do 1.00 M i $c_{AgNO_3} = 1.0 \times 10^{-6}$ M do 2.00 M udio kubičnog i heksagonalnog AgI kompleksno se mijenja. Pokazano je da se čista heksagonalna modifikacija formira samo uz 'suvišak' KI koncentracije 1,00 M. Smanjenjem koncentracije suviška KI do pI 4, procent heksagonalnog AgI pada na 22% a nakon daljnjeg smanjenja koncentracije KI postotak heksagonalnog AgI opet raste. Iz vodenih otopina sa suviškom AgNO₃ (od 1.0×10^{-6} M do 2,00 M) ne može se precipitacijom dobiti čisti kubični AgI, već maksimalno 80% uz pAg 1 do 2. Starenjem rastu kristaliti AgI, no odnos kristalnih modifikacija se ne mijenja. Brzina dodavanja precipitacionih komponenata različito utječe na disperzitet i udio kristalnih modifikacija AgI. Disperzitet i postotak kristalnih modifikacija AgI različito su ovisni o koncentraciji jedno i dvovalentnih koagulacionih iona. Kiselost medija u intervalu od $pH = 0.1$ do $pH = 5,8$ ne utječe znatno na disperzitet i udjele kristalnih modifikacija AgI. Površinski aktivne supstance u koncentracijama od 1.0×10^{-7} M do 1.0×10^{-5} M utječu samo na disperzitet sola, a ne i na kristalnu strukturu čestica sola. Ako se otopina AgI u AgNO₃ razrijedi vodom, formiraju se solovi AgI u kojima je to više kubičnog AgI, što je niža koncentracija otopine AgNO₃ u kojoj je AgI bio otopljen. Razređivanjem otopina AgI, koji je otopljen u KI, formiraju se solovi u kojima je to više heksagonalnog AgI što je bila niža koncentracija otopine KI u kojoj je AgI otopljen prije razređivanja. Hlađenjem kompleksno otopljen AgI u 2,0 M KI s temperature 160⁰ C na sobnu temperaturu (0,2⁰/min.), formiraju se prozirni 100% kubični kristali AgI.

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