X-Ray Diffraction Analysis of Dried AgI Prepared by Isoelectric Coagulation

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AgI is prepared by isoelectric coagulation. The rapidity of precipitation is 10 and 1000 minutes respectively. Prior to washing the isoelectric AgI precipitate is aged for 10 or 1000 minutes in isoelectric supernatant liquor. By washing spherical AgI aggregates are formed the size of which is 1—3 mm. AgI is then dried. A part of dried isoelectric AgI is crushed. The crushed and not crushed AgI is separately sieved passing through silver sieves (30—60 mesh). Sieved AgI is analysed using the *Philips* X-Ray diffractometer.

The X-ray diffraction analyses show that rapidity of precipitation and the aging process in isoelectric mother liquor as well as the crushing process do not essentially influence the ratio of crystallographic α- and β-AgI modifications.

By a rapid (10 minutes) coagulation and by short aging time (10 minutes) AgI precipitate containing 57—58% of cubic α-AgI (42—43% hexagonal β-AgI) is formed; by a rapid (10 minutes) coagulation and by long aging time (1000 minutes) AgI precipitate containing 52—54% of cubic α-AgI (46—48% hexagonal β-AgI) is formed, and by slow precipitation (1000 minutes) and short aging time (10 minutes) a precipitate with 55% of cubic α-AgI (45% hexagonal β-AgI) is formed. The highest difference in the ratio of α- and β-AgI in crushed and not crushed AgI is as low as 2%.

INTRODUCTION

The results of the investigations of crystallographic structure of AgI precipitated show that the AgI precipitate is of a cubic (α-AgI) or hexagonal (β-AgI) structure. The AgI precipitate formed in the presence of an excess of I⁻-ion is hexagonal β-AgI. The AgI precipitate formed in the presence of an excess of Ag⁺-ion is cubic α-AgI. By an equivalent precipitation AgI precipitated is a mixture of α and β-AgI. By intensive crushing of cooled, melted AgI (β-AgI), β-AgI is transformed to cubic α-AgI[1-3].

The dried isoelectric AgI precipitates, precipitated at different rapidities and aged for different aging times in isoelectric mother liquor show different adsorption capacity in dependence on precipitation rapidity and aging time in isoelectric mother liquor[4]. The rapidity of the heterogeneous AgI-I⁻ (¹³¹I) process shows also the dependence on the same parameters[4]. The crystallite size of AgI is found to be an important parameter determining the adsorption capacity and the capacity of the heterogeneous exchange process respectively. By aging the AgI crystallites are increased in size and transformed into a more stable crystallographic modification[5].

The crystallite size of the precipitate depends on the rapidity of precipitation. During precipitation particles of the formed solid phase are structurally transformed into a more stable crystallographic form (unless, of course, the precipitation process is too fast). Since these parameters are important for the analysis of the adsorption and heterogeneous exchange processes, in the present paper an investigation of the influence of the rapidity of precipitation and of aging time of the precipitates in the isoelectric supernatant liquor on the proportions of α and β modifications of AgI in the isoelectric precipitate is described.

<center>EXPERIMENTAL</center>

Preparation of dried isoelectric AgI

Dried isoelectrically precipitated AgI was prepared by adding AgNO₃ (0.050 M) from a pipet to agitated NaI (2 1, 0.050 M) solution. The AgNO₃ solution was added during $t_p = 10$ and 1000 minutes respectively. The point of equivalence was determined potentiometrically (*Radiometer* M 4) by using the indicator Ag/AgI rotating electrode[6,7] in plug with the standard Hg/Hg₂SO₄ electrode. As the equivalence point the region between $6.2 > pAg > 6.0$ was used. The AgI precipitate was agitated during $t_g = 10$ and 1000 minutes respectively in the isoelectric supernatant liquor (~ 150 ml.) and washed by twice distilled water (15×150 ml. approximately) until the washings showed a constant electric conductivity (*Cambridge Conductivity Bridge* — 43921). AgI was then vacuum dried (2 mm Hg, for 70 hours), and one part of the dried AgI precipitate was crushed in a mortar and passed through silver sieves of 30—60 mesh.

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 α 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 cubic and hexagonal modification respectively were recorded. Sometimes we also used hexagonal line (101) at $\Theta = 12.7^0$. The squares of the structure factor magnitudes 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 respectively.

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)[8] 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 prefered orientation of the crystallities could be neglected, because the fluctuations of the results were less than 2⁰/₀. This conclusion was
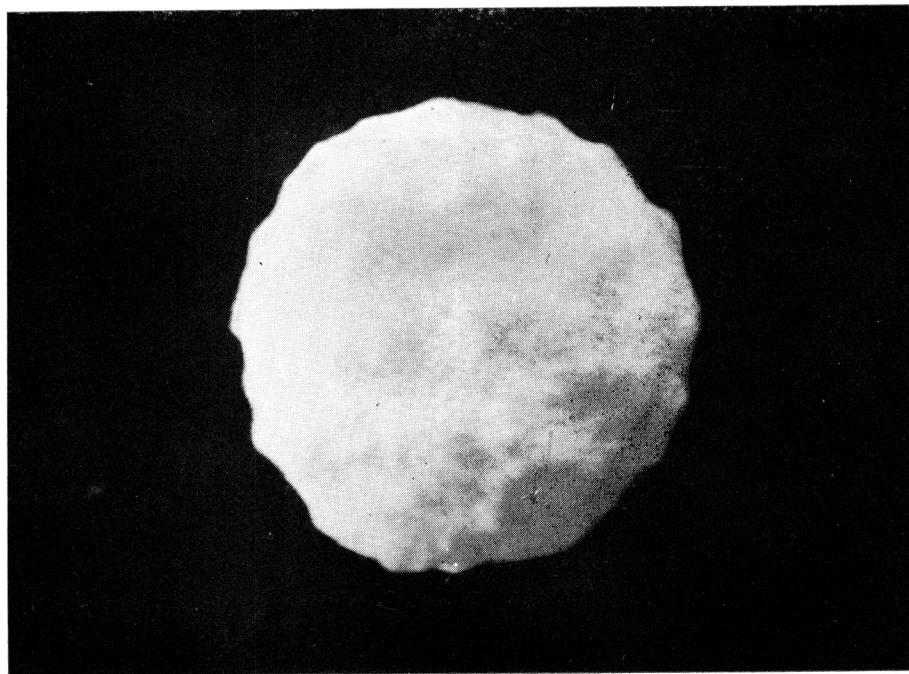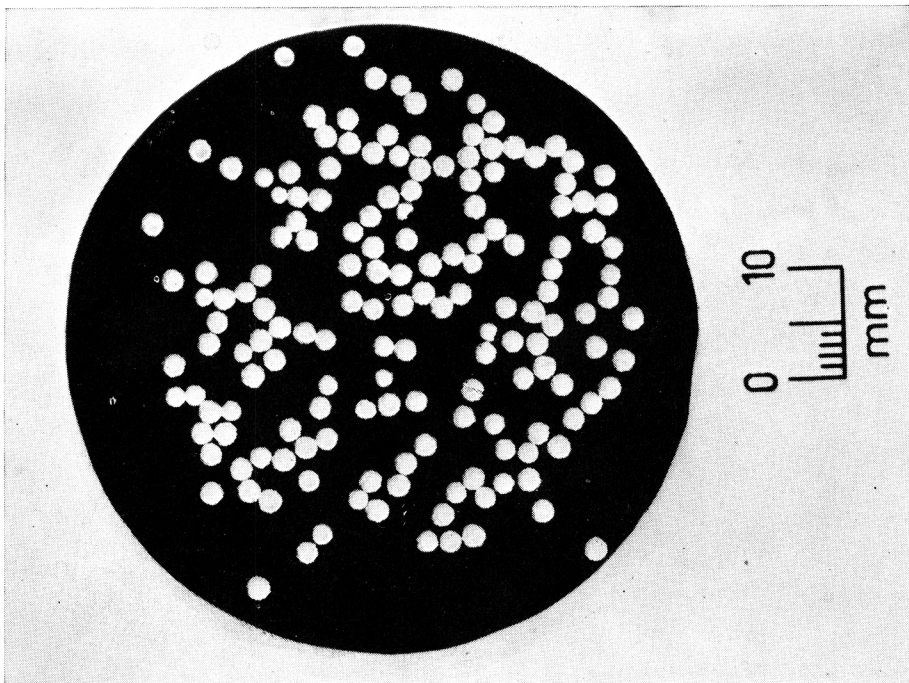
Fig. 1. Dried isoelectric AgI.
Left — spherolitic aggregate with particle size 1—3 mm, formed by washing after one day mixing of the precipitate in water by which AgI is rinsed.
Right — the same magnified 20 ×.

confirmed also 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 the known Scherrer's formula using the angular breadths of the lines where the intensity is half its maximum value. 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 with no crystallite size broadening. The pure diffraction breadths were deduced by the use of Alexander's correction curves[9].

RESULTS

The isoelectric maximum of AgI—NaI systems lies in the positive region[6] between $6.2 > pAg > 5.7$.

The end point of the isoelectric AgI precipitation is here led to $6.2 > > pAg > 6.0$. By washing the precipitate after aging in supernatant liquor, final AgI powder is formed (with crystallite size from 70 up to 300 mμ). If the washing is carried out for a longer time and if the system is agitated, a spherolytic aggregate is formed (Fig. 1.). The diameter of the spherolytes is 1—3 mm. In spherolytic aggregate individual particle size of AgI is larger than 200 mμ.

Our results, which are in accordance with the data of other authors[1,2], show that AgI formed by isoelectric precipitation is an approximately equivalent mixture containing cubic α-AgI and hexagonal β-AgI. The influence of the rapidity of precipitation and aging (in isoelectric supernatant liquor) on the proportion of crystallographic α- and β-AgI modifications (Table I) is very small. The results also show that crushed and not crushed AgI precipitates are crystallographically much the same. In all cases cubic α-AgI is present in small excess. Small structural differences between the crushed and not crushed solid AgI show a slight influence of crushing on the exchange of the ratio of crystallographic α- and β-modifications of AgI. These results are not in opposition to experiments showing that by strong crushing cubic α-AgI is formed from hexagonal β-AgI[3]. For crushing melted AgI much more mechanical work is needed than for crushing dried isoelectric precipitate. That is why structural transformations of β- to α-AgI in our experiments are so small.

TABLE I

No.	t_p (min.)	t_g (min.)	Crushed AgI	K %
1	10	10	—	57
2	10	10	+	58
3	10	1000	—	54
4	10	1000	+	52
5	1000	10	—	55
6	1000	10	+	55

Dried AgI formed by isoelectric precipitation. The precipitation process is carried out for $t_p = 10$ (samples No. 1—4) and 1000 minutes (samples No. 5 and 6) respectively. Precipitated AgI is aged for $t_g = 10$ and 1000 minutes respectively in isoelectric supernatant liquor prior to washing and drying. Prior to X-ray analysis the AgI precipitate is crushed (denoted by +) or not crushed (denoted by —) and pased through silver sieves (30—60 mesh). X-ray data are represented as per cent of cubic α-AgI (K %) in analysed samples.

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IZVOD

Rendgenska analiza sušenog AgI priređenog izoelektričnom koagulacijom

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Različitim brzinama (10 ili 1000 minuta) kontinuirano je taložen AgI (oko 2 l 0,050 M AgNO$_3$ u 2 l 0,050 M NaI) do izoelektrične tačke (6,2 > pAg > 6.0). Prije ispiranja AgI 'stari' 10 ili 1000 minuta u izoelektričnoj matičnici, a zatim je ispiran bidestiliranom vodom (cca 15 × 150 ml) do konstantne vodljivosti vode od ispiranja. Opran AgI je sušen u vakuumu (2 mm Hg) kroz 70 sati na temperaturi od 50° C. Jedan dio taloga je smrvljen i prosijan kroz srebrno sito (30—60 mesh). Nesmrvljen dio je također prosijan kroz isto sito. Pomoću Philipsovog difraktometra analiziran je odnos kristalografskih α- i β-modifikacija AgI. Rezultati pokazuju, da brzina precipitacije (10 ili 1000 minuta) i proces 'starenja' u izoelektričnoj matičnici, kao i mehanički proces drobljenja praktično ne utječu na promjenu odnosa kristalografskih modifikacija u AgI, jer se u svim a različito tretiranim uzorcima količina kubičnog α-AgI kreće u granicama od 52 do 58⁰/o (heksagonski β-AgI 42—48⁰/o). Odnos α prema β modifikaciji AgI u izoelektričnom precipitatu mijenja se najviše za 6⁰/o, bez obzira kojom je brzinom AgI precipitiran, ili koje je vrijeme staren u izoelektričnoj matičnici. Zbog drobljenja se odnos kristalografskih α- i β-modifikacija mijenja najviše do 2⁰/o. Prema tome ovi rezultati pokazuju da u ispitanim uvjetima brzina precipitacije i starenje u izoelektričnoj matičnici kao i proces mrvljenja ne dovode do značajnije promjene odnosa kristalografskih modifikacija u AgI partikulama.

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