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## X-Ray Diffraction Analysis of Differently Prepared AgI. IV

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The cubic/hexagonal ratio of AgI formed by dilution of a solution of silver iodide in NaI and AgNO<sub>3</sub> solutions respectively, and the cubic/hexagonal ratio of AgI formed *in statu nascendi* in mixed solvents has been investigated. The complex solution of AgI + NaI (1, 2, 3, 4, and 8 M NaI) was diluted with water to 0.01 M NaI. The formed mixtures of cubic and hexagonal AgI contained less cubic AgI in systems of lower initial concentrations of NaI as compared with those of higher initial concentrations of NaI. By an increase in the amount of AgI at constant NaI concentration the amount of cubic AgI decreased: by aging this amount increased. By dilution of a complex solution of AgI + AgNO<sub>3</sub> a larger amount of cubic AgI was formed when the initial concentration of AgNO<sub>3</sub> was lower (1 M as compared to 8 M AgNO<sub>3</sub>).

In AgI sols prepared in water-methanol and water-ethanol mixtures, the amount of cubic and/or hexagonal modifications of AgI changes, by an increase in the percentage of alcohol, in another way than it does in water-dioxane and water-acetone systems. By comparing the changes of the dielectric constant of the medium, the surface tension and the solubility of AgI it can be concluded that complexly dissolved AgI is probably the factor which most influences the formation of a  $\alpha$  or  $\beta$  structure of AgI.

### INTRODUCTION

The results obtained in previous papers of this series<sup>1,2</sup> show that the percentage of cubic and hexagonal modifications and crystallites size of precipitated and coagulated AgI depend on the concentration and chemical nature of the electrolytes present in the system. On the other hand the heterogeneous exchange processes AgI—I<sup>-</sup> and AgI—Ag<sup>+</sup> which are caused by Ostwald ripening process and/or by selfdiffusion of Ag<sup>+</sup> and I<sup>-</sup> ions respectively show that the exchange rate on coagulated AgI sols is different from that on stable AgI sols<sup>3</sup>. The cubic/hexagonal ratio, K/H, which is important in elucidation of the mechanisms of heterogeneous exchange on stable AgI sols has been studied. Differently prepared stable AgI sols have been analysed using the X-ray diffraction technique and the results are described in this paper.

### EXPERIMENTAL

#### Materials

Analar grade chemicals (BDH, Merck, Fluka) were used throughout the experiments. Iodine-131 was obtained from the Nuclear Institute Vinča (Yug), as a solution of carrier free <sup>131</sup>I<sup>-</sup> of the NaI form. Twice distilled water, the second time from an all-Duran still and regularly tested for conductivity, was used.

### Preparation of Sols

The following designations are used for the silver iodide sols:

- a) — sol A, silver iodide prepared by diluting the complex solution of 25.0 ml. 8.00 M AgNO<sub>3</sub> + 4 g. AgI;
- sol B, silver iodide prepared by diluting the complex solution of 25.0 ml. 4.00 M AgNO<sub>3</sub> + 2 g. AgI;
- sol C, silver iodide prepared by diluting the complex solution of 25.0 ml. 2.00 M AgNO<sub>3</sub> + 2 g. AgI;
- sol D, silver iodide prepared by diluting the complex solution of 25.0 ml. 1.00 M AgNO<sub>3</sub> + 1 g. AgI.

After dilution of the initial complex solutions the concentration of AgNO<sub>3</sub> in the A, B, C, and D sols was 0.100 M.

- b) — sol E, silver iodide prepared by diluting the complex solution of 25.0 ml. 8.00 M NaI + 20 g. AgI;
- sol F, silver iodide prepared by diluting the complex solution of 25.0 ml. 4.00 M NaI + 11 g. AgI;
- sol G, silver iodide prepared by diluting the complex solution of 25.0 ml. 2.00 M NaI + 2 g. AgI;
- sol H, silver iodide prepared by diluting the complex solution of 25.0 ml. 1.00 M NaI + 1 g. AgI.

After dilution of the initial complex solutions the concentration of NaI in E, F, G and H sols was 0.100 M.

- c) — sols J, silver iodide sols prepared in essentially the same manner as that described elsewhere<sup>2,3</sup> by precipitation reaction *in statu nascendi*. The stable sols of AgI thus obtained were aged prior to X-ray analysis one day and thirty days, respectively;
- sols K, silver iodide sols prepared by adding a 50.0 ml. 0.020 M silver nitrate solution to a 50.0 ml. 0.040 M sodium iodide solution. Silver nitrate and sodium iodide were dissolved in water and/or water-dioxane mixtures containing 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% dioxane;
- sols L, silver iodide sols prepared in the same way as sols K, in water-acetone mixtures containing 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% acetone;
- sols M, silver iodide sols prepared in the same way as sols K, in water-methanol mixtures containing 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% methanol;
- sols N, silver iodide sols prepared in the same way as sols K, in water-ethanol mixtures containing 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% ethanol.

### X-ray Diffractometry

All systems were thermostated at  $293.0 \pm 0.1^\circ$  K using a Haake ultrathermostat. Stable sols aged for 1 and 30 days respectively were settled by centrifugation using a superspeed automatic Servall centrifuge; then small quantities of the supernatant containing the sol were placed in a sample holder of a Philips diffractometer.

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

The conditions under which the X-ray analysis was performed were described in detail in earlier papers<sup>12</sup>.

The hexagonal diffraction line (100) at the Bragg angle  $\Theta = 11.2^\circ$ , and overlapping diffraction lines (111) and (002) at  $\Theta = 11.9^\circ$  of the cubic and hexagonal modification were recorded. Sometimes we also used hexagonal line (101) at  $\Theta = 12.7^\circ$ .

*Surface Tension Analysis*

The surface tension at the interface liquid/air was determined by a thermostated Ostwald stalagmometer. The mean of the counted drops of five samples was taken as the result using water as the standard.

*Radiometric Determination of the Solubility of AgI*

The determination of the solubility of AgI in a 0.010 M NaI + 0.4 M NaNO<sub>3</sub> mixture dissolved in water and 10% to 80% (vol/vol) acetone-water and dioxane-water solvents respectively was carried out using an already described<sup>4</sup> standard radiometric technique. The silver iodide sol was prepared using the precipitation reaction obtained by adding the silver nitrate solution to labelled sodium iodide solution containing sodium nitrate, all in an adequate solvent. Counts were taken by means of an Ekco Electronics scaler connected with a well type NaI(Tl) scintillation counter. All radiometric measurements were carried out using carrier free <sup>131</sup>I of the NaI form. The solubility of AgI was calculated on the basis of the distribution of radioiodine in the AgI-NaI system. If the total concentration of iodide present as solid phase is  $n^s$ , and the total concentration of iodide in liquid phase  $n^l$ , then the distribution of iodide in the system is  $\alpha = n^s/n^l$ , from which the solubility of AgI has been calculated.

## RESULTS

The results summarized in Table I show the influence of the initial concentration of AgNO<sub>3</sub> and NaI, and of the amount of AgI dissolved on the amount of cubic AgI formed by dilution of the concentrated complex solution to 0.10 M AgNO<sub>3</sub> and 0.10 M NaI, respectively. At higher initial concentration of AgNO<sub>3</sub> the amount of cubic AgI formed was smaller than at low initial concentration of AgNO<sub>3</sub> in complex solution of AgI sols aged 1 and 30 days respectively. By aging the K/H ratio was changed. The influence of high initial concentration of NaI on the K/M ratio in 30 days aged AgI sols exhibits an opposite effect to that in systems with high initial concentration of AgNO<sub>3</sub>.

TABLE I  
X-Ray Diffraction Results

AgI sol type:	Percentage, K %, of cubic AgI aged at $T = 293.0 \pm 0.1^\circ$ K for	
	1 day	30 day
a) Silver iodide sol prepared by dilution of the complex solution of AgI in silver nitrate solution:		
A	43	33
B	52	43
C	68	66
D	80	88
b) Silver iodide sol prepared by dilution of the complex solution of AgI in sodium iodine solution:		
E	43	64
F	54	57
G	41	44
H	33	29

The influence of the amount of AgI on the K/H ratio in the AgI sols containing an excess of sodium iodide is shown in Table II. By an increase in the  $n^S/n^L$  ratio in 1- and 30-days-aged AgI sols the percentage of cubic AgI markedly decreases in the solution containing 0.100 M NaI. In other systems containing an excess of NaI ( $10^{-4}$  M to  $10^{-2}$  M) there is no consistent change larger than the differences between the results obtained on various systems.

TABLE II  
X-Ray Diffraction Results

Percentage, K % of a cubic silver iodide in the sol of type J, aged for 1 day and 30 days ( $t_A$ ) at  $T = 293.0 \pm 0.1^\circ$  K:

$t_A$	$n^S/n^L$	K %
1	0.10	77
1	1.00	65
1	10.0	39
30	0.10	84
30	1.00	70
30	10.0	43

Crystallographic characteristics of AgI in stable sols formed in water-dioxane solutions depend on the amount of dioxane in the mixture (Fig. 1). The maximum percentage of cubic AgI (100%) is reached in 30-days-aged sols in systems containing up to 40% of dioxane. In systems aged for 30 days and containing 50% and 60% of dioxane about 100% of cubic AgI was formed. In systems containing more than 60% of dioxane the percentage of cubic AgI decreased to about 60%. On 1-day-aged stable AgI sols in water-dioxane solutions about 60% of cubic AgI was formed. The surface tension at the air/solution boundary decreased from 72 dynes/cm in water solutions to 37

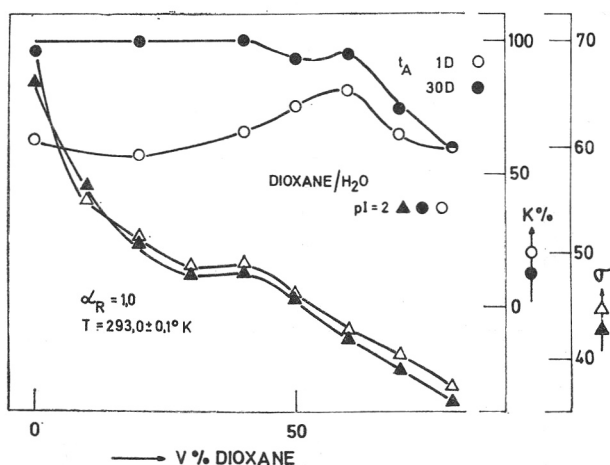


Fig. 1. Percentage, K%, of cubic silver iodide and surface tension ( $\sigma$  dynes/cm) of solution/air plotted against the volume percentage, V%, of dioxane in water.



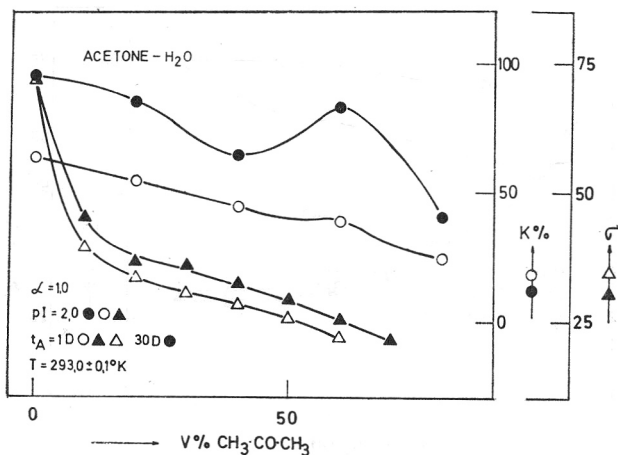


Fig. 2. Percentage, K%, of cubic silver iodide and surface tension ( $\sigma$  dynes/cm) of solution/air plotted against the volume percentage, V%, of acetone in water.

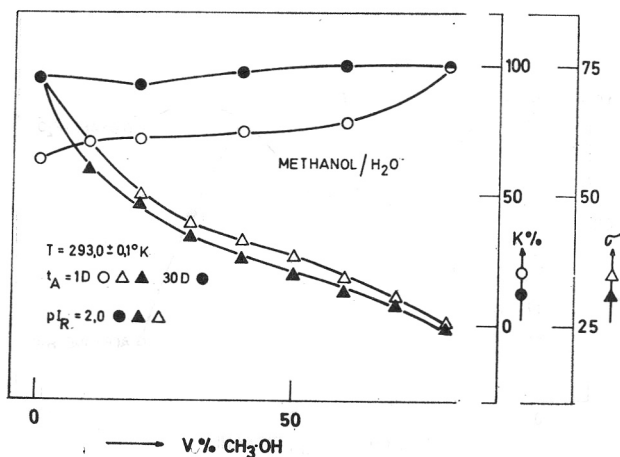


Fig. 3. Percentage, K%, of cubic silver iodide and surface tension ( $\sigma$  dynes/cm) of solution/air plotted against the volume percentage, V%, of methanol in water.

dynes/cm in the solution containing 80% of dioxane. In systems containing 70% and 80% of acetone (Fig. 2) the surface tension decreased from 72 dynes/cm to about 23 dynes/cm. In these systems, the percentage of cubic AgI decreased when the concentration of acetone in the solution is increased. By aging the sols, the percentage of cubic AgI formed was increased. The surface tension of AgI sols containing methanol or ethanol (Figs. 3, 4) decreased from 72 dynes/cm in water to about 25 dynes/cm in systems containing 80% methanol or ethanol. When the percentage of alcohol was increased from 0% in 1-day-aged AgI sols the amount of cubic AgI was larger at higher concentration of alcohol in the solution (60% to 100% cubic AgI). In all systems aged for 30 days about 100% of cubic AgI was present. The results of the

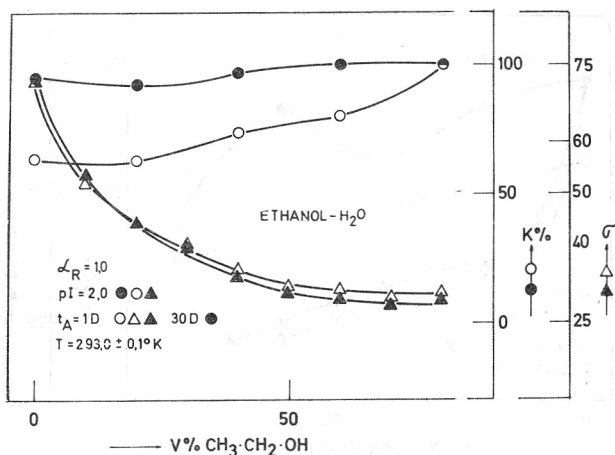


Fig. 4. Percentage, K%, of cubic silver iodide and surface tension ( $\sigma$  dynes/cm) of solution/air plotted against the volume percentage, V%, of ethanol in water.

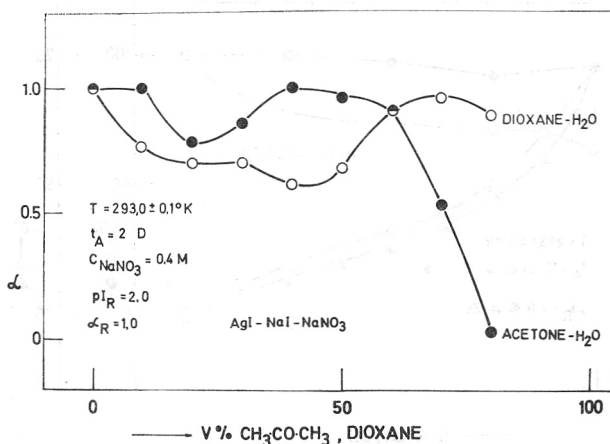


Fig. 5. Solubility of silver iodide plotted against the volume percentage, V%, of acetone and/or dioxane in water. Ordinate:  $\alpha = n^S/n^L$  where  $n^S$  = the amount of iodide in the solid phase (AgI sol),  $n^L$  = the amount of iodide in the liquid phase (NaI solution + dissolved silver iodide complex).

radiometric determination of the solubility of AgI in water-dioxane and water-acetone solutions, of a 0.010 M NaI solution show (Fig. 5) the dependence of solubility of AgI on the solvent composition. In all cases the solubility was higher in mixed solvents than in pure water. In 80% acetone containing 0.010 M NaI, silver iodide (0.010 M/l AgI) was completely dissolved.

#### DISCUSSION

The results obtained in this work show complex dependence of the K/H ratio on the conditions of preparation of stable AgI sols. The influence of the initial concentration of  $\text{AgNO}_3$  and NaI on the K/H ratio in the AgI sols

obtained by dilution with water is the same as already described<sup>2</sup>. This is normal because when a very concentrated complex of silver iodide is diluted (at initial generation of solid phase) it influences, by its steric configuration, the crystal structure of AgI. This being also in good agreement with Težak's concepts<sup>5</sup> of interrelation and interaction between the constituent ions in the liquid phase and the chemical and physical properties of the formed solid phase. Since the quantity of solid phase in the AgI sol is one of the important factors influencing the formation of the solid phase, it should be reflected on the K/H ratio in the systems containing various amounts of AgI. Analogously, in such systems at constant excess of 0.100 M NaI, the percentage of cubic AgI depends on the amount of AgI: when AgI is present in low concentrations, the cubic modification is formed in large amounts, when AgI is present in high concentration, the amount of cubic AgI is small (Table II). Under the same conditions, the amount of cubic AgI is increased by aging the sols, this being a consequence of the transformation of the unstable hexagonal to the stable cubic crystal modification of AgI. In systems containing a small excess of NaI ( $10^{-4}$  M to  $10^{-2}$  M) the total amount of the solid phase in the sol is so small that it does not influence the K/H ratio. In coagulated AgI sols aged for 30 days no changes of the cubic into the hexagonal modification of AgI and vice versa are observed<sup>2,7</sup>. This shows that there is a difference between the properties of stable and coagulated AgI sols. This is important for the elucidation of the role of coagulating ions adsorbed on the surface of the solid AgI.

On the basis of different electrokinetic behaviors of differently prepared monodisperse silver halide sols Ottewill assumed, as a reasonable conclusion, that the electrokinetic properties of silver halide sols are influenced by the solid state properties of the crystals<sup>8</sup>. It is also known that the K/H ratio<sup>2,7</sup> depends on the concentration and valency of the cations and anions in the AgI sols. The heterogeneous exchange experiments and adsorption-desorption equilibria measurements on differently precipitated isoelectric silver iodide sols show<sup>9</sup> that neither the adsorption capacity of AgI nor the rate of the exchange process are constant: on fastly precipitated AgI, which contains more crystal disorders, the adsorption capacity as well as the rate of the exchange process are higher than on slowly precipitated AgI. This directly indicates the role of crystal disorders in the adsorbed amount of coagulating ions. Also it points out that the imperfection in the crystal space of AgI in the sol is essential for the mechanisms of the exchange process, *i. e.* for Ostwald ripening. It seems that an equilibrium is established between the adsorbed ions and the imperfections in the crystal space. In this way we can explain the fact that in the coagulated AgI sol the transformation from hexagonal to cubic AgI is not so fast as it is in stable sols. All this indicates that the solid-state properties in the crystal space directly depend on the medium in which AgI is formed and also that the interaction with the bulk of the solution is in connection with solid-state properties of the crystal space, which is in good agreement with the above mentioned conclusion by Ottewill<sup>8</sup>. Under these conditions the colloid-chemical properties of silver halide sols depend on the dielectric constant of the liquid phase<sup>6</sup> and therefore the K/H ratio was determined on several systems of stable AgI sols containing solvents with different dielectric constants (Figs. 1—4). In water-dioxane, water-methanol and

water-ethanol solvents a larger amount of cubic AgI is formed in 30 days aged sols than in one day aged sols. In water-acetone all values are much smaller. In all systems the dielectric constant increases when the concentrations of the mentioned solvents is decreased and the surface tension of the liquid/air interface decreases too. The concentration of the surfactants influences the variation of surface tension, viscosity, conductance *etc.* in the same range of concentration in which it influences also the variation of zeta potential, adsorption capacity, heterogeneous exchange rate *etc.* in contact of the same solution with a solid phase<sup>3,10</sup>. In the systems containing dioxane and acetone, besides the dielectric constant and the surface tension, the solubility of sols does also change (Fig. 5). Therefore each solvent composition has a different solubility equilibrium causing different states in the methorical layer. The situation in systems containing acetone or dioxane is not so simple as in those containing alcohols. In water-alcohol mixtures silver iodide is sparingly soluble, and when the concentration of alcohol in the system is increased the solubility of AgI still decreases<sup>11</sup>. Thus we can conclude that in systems containing dissolved AgI (80% alcohol, Figs. 3, 4), *i. e.* in systems where AgI is probably not present in another complex form, it will be formed as stable cubic silver iodide. This shows the role of the chemical nature of the bulk solution, particularly the role at chemical and stereochemical factors determining the solid state properties of silver iodide. The solubility of AgI in mixed solvents is not influenced by the dielectric constant<sup>11</sup>. In the investigated systems the dielectric constant as well as the surface tension decrease when the percentage of nonaqueous solvent increases while the solubility of AgI and the K/H ratio under such conditions are different. Since there is no parallelism between the influences of the dielectric constant and the surface tension in systems on the K/H ratio, we assume that the stereochemical factors of silver iodide complexes play a more important role in determining the properties of the solid phase than other observed parameters.

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## IZVOD

**Rendgenska analiza različito pripremanog AgJ. IV.***R. Despotović, Z. Despotović, M. Mirnik i B. Subotić*

Istraživan je udio kristalnih modifikacija, kubičnog i heksagonalnog AgJ koji nastaje razrjeđivanjem kompleksnih otopina AgJ i NaJ i  $\text{AgNO}_3$  te pripremanog »in statu nascendi« u smjesama otapala. Otopine AgJ u 1, 2, 4 i 8 M NaJ razrjeđivane su vodom do 0.10 M NaJ; formiraju se smjese kubičnog i heksagonalnog AgJ u kojima je udio kubičnog AgJ to manji što je manja početna koncentracija NaJ. S porastom količine AgJ, uz konstantnu koncentraciju NaJ, pada udio kubičnog AgJ; starenjem formiranog AgJ raste udio kubične modifikacije. Razrjeđivanjem otopina AgJ otopljenog u  $\text{AgNO}_3$  formira se AgJ s to većim udjelom kubičnog AgJ, što je manja početna koncentracija  $\text{AgNO}_3$ .

U AgJ solovima, pripremanim u smjesama otapala voda/metanol i voda/etanol, udio kubične, odnosno heksagonalne modifikacije AgJ drugačije se mijenja s povećanjem procenta alkohola, nego u sistemima voda/dioxan i voda/acetone. Uspoređivanjem promjene dielektrične konstante medija, napetosti površine i topljivosti AgJ zaključuje se da je vrlo vjerojatno kompleksno otopljeni AgJ najznačajniji faktor tekuće faze koji utječe na formiranje određene strukture AgJ.

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