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Synthesis of Silver Halide Tabular Crystals—The Effect of the Solvent on the Stability of {111} Faces

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Silver bromide crystals have been precipitated by the double-jet method. The presence of polar aprotic solvents or protic solvents with a dissociation constant smaller than water increased the ratio and size of tabular crystals in the precipitate. This is explained considering that {111} surfaces are mainly composed of halide ions and therefore charged. Organic solvents reduce the solvation of the halide ions in the solution and stabilize the surface charge. A high ionic strength greatly favored the ratio of tabular crystals and enhanced tabular growth probably by helping the formation of the double electrical layer on the charged {111} faces.

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Introduction

Silver halide tabular crystals are mainly bounded by {111} faces and they include several {111} twin planes. The production of those crystals requires crystallization conditions favoring twinning events and a media in which {111} faces are the most stable. Silver chloride and bromide crystallize with a rock-salt structure. A full {100} surface in a crystal with this structure is composed of a smooth layer containing the same amount of cations and anions where every ion is linked to four ions of different sign within the same layer. However, a complete {111} surface is only composed of ions of the same sign so the ion interactions within a layer will be repulsive and the surface will have a net dipole moment. According to the Hartman–Perdok theory, {100} faces should be the most stable in crystals with the rock-salt structure, while {111} faces, which are kink faces, are very unlikely to appear on real crystals.[1] Actually, {100} are the only faces appearing on alkaline halide and silver halide crystals grown from the melt. The same holds for crystals grown in pure solutions at moderate supersaturation. However, when supersaturation increases above a critical value {111} faces become dominant in alkaline halides.[2] This critical value can be substantially lowered by the presence of additives like urea and many divalent cations (Cd^{2+}, Mn^{2+}, Pb^{2+}, etc.). Certain solvents can also induce the presence of {111} faces. For instance, NaCl crystals develop {111} faces when they are grown in formamide.[3]

This is a study about precipitating media that favor the formation of {111} faces in silver halide crystals with the aim of enhancing the production of tabular crystals. First, conditions favoring the stability of {111} faces were analyzed theoretically. Then, silver halide crystals were precipitated by the standard double-jet method in several media containing mixtures of polar solvents and also in high-ionic-strength media. It is shown that the medium has an important influence in the number, size, and aspect ratio of tabular crystals in the precipitate.

Silver Halide Complexes

In aqueous media, growing AgBr crystals develop the {111} form, when the excess of the halide ion in the media gets larger than 10^{-3} mole/L. At these conditions, a large proportion of the silver contained in the solution is in the form of charged halide complexes (Fig. 1). But {111} faces adsorb bromide ions when they are in excess.[4] Admitting that the silver halide charged complexes are the main silver source for crystal growth at these conditions, the repulsion between those complexes and the {111} surface would explain the slow growth of {111} faces. In this way, silver halide charged complexes often are considered responsible for the formation of {111} faces and the occurrence of twinning.[6,7] Following this line, one should look for solvents in which silver halide complexes are very stable to obtain tabular crystals. Formation constants of silver halide complexes change[8] with the solvent in a different way for each halide ion (Table I). (1) In water, the formation constant of silver halide complexes increases substantially when going from chloride to bromide and then to iodide. (2) In protic solvents with a dissociation constant smaller than water, the values of silver complex formation constants for the three halides get closer. In mixtures water–ethanol solubility products decrease while complex formation constants increase with the ratio of ethanol in the mixture (Fig. 2). (3) In polar aprotic solvents, the values of complex formation constants are practically the same for the three halides and they are several orders of magnitude higher than those in water. This behavior can be explained by the relatively strong solvation of chloride ions in water, owing to the formation of hydro-

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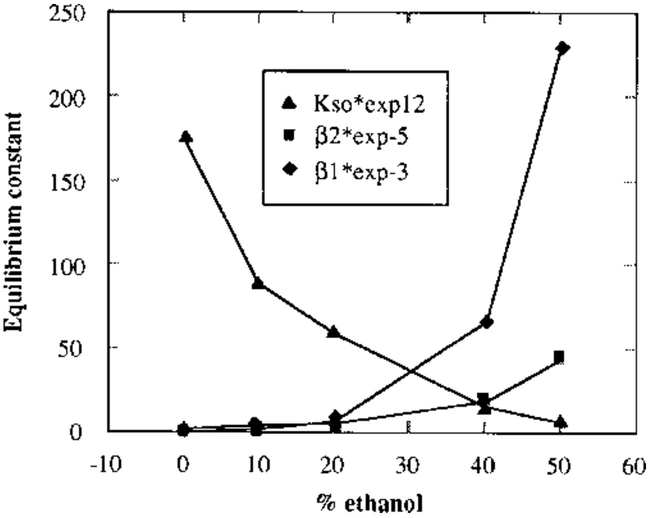


Figure 1. Variation of the molar fraction of silver bromide complexes in solution and the total concentration of charged silver bromide complexes (thick line) with the pBr (-log[Br$^-$]) and domains of precipitation of the several crystal morphologies (equilibrium constants at 50°C, from Ref. 5).

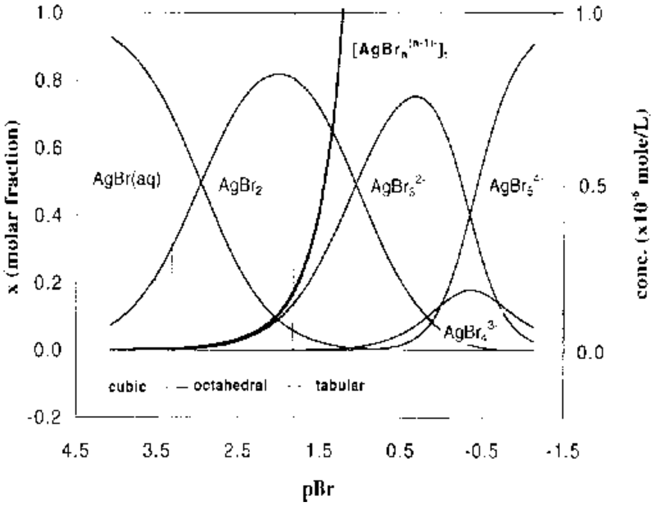


Figure 2. Variation of the solubility product of silver chloride and the formation constants of the AgCl and $AgCl_2$- complexes in water–ethanol mixtures with the ratio of ethanol in the mixture (equilibrium constants at 25°C, from Ref. 21).

gen bonds.[9] Bromide and iodide ions are weaker H-bond acceptors than chloride ions due to their larger size and lower electronegativity. So, silver chloride has a relatively high solubility in water and silver chloride complexes have a low stability. Aprotic solvents cannot form H-bonds. They can link to halide ions through ion–dipole interactions. Those interactions are equally weak for all the halide ions so the solubility of their silver salts is similar. But the interactions of the solvent with the complex ions will have a dipole–dipole nature. Thus, silver halide complexes will be better solvated in polar aprotic solvents than in water, if the dipolar moment of the solvent is higher than that of water.

Structure of {111} Faces

The stacking of the ions along the [111] crystallographic direction in the rock-salt structure consists of alternating layers of ions with the same charge. Keeping the same structure as in the bulk and being isolated, a complete {111} surface would have a neat electrical charge and a dipole moment.[10,11] The real atomic disposition of {111} faces is still unknown. It has been shown that they may exhibit surface reconstruction.[12,13] Models have been proposed that explained the measurements on epitaxial {111} surfaces by surface decoration methods.[14] Those methods are based on neutral arrangements of ions and vacancies on the topmost layer. In crystals grown in solution, however, it has been found that {111} surfaces may contain an excess of the halide ion.[15] Surface conductivity measurements[16] and values of Z-potential also point to a surface composed by halide ions with double electrical layers on both sides of the solid–liquid interface.[17] Recently, x-ray photoelectron spectroscopic studies[18] confirmed that there is a high excess of bromide ions in the outer {111} surfaces, especially on tabular crystals. Thus, we may consider that {111} surfaces are mainly composed of halide ions and they have a neat charge. Therefore, the stability of {111} faces can be enhanced by the solvent: (a) when the interaction of the solvent with the halide ions is weak and (b) when the action of the solvent on the surface compensates the effect of the neat charge. Water is not well suited for this purpose because it binds strongly to the halide ions by H-bonds. This is especially true for chloride ions and that must be why the {111} form is so rare on silver chloride crystals. Polar aprotic solvents interact weakly with halide ions and they can have a high dipolar moment so they can bind to {111} polar surfaces. Therefore, polar aprotic solvents are expected to enhance octahedral and tabular crystals. The use of these solvents in the production of silver halide tabular emulsions has been patented.[19] An extensive adsorption of foreign ions forming a double charged layer upon these surfaces would compensate this charge and help stability. Therefore, tabular crystals would be favored in media with a high ionic strength. This point has been proven in seeded experiments at low pBr.[20]

Experimental

A standard double-jet method was used in the experiments. The precipitation was always carried out in a 1-L double coated steel crystallizer with a two-blade metallic stirrer turning at a speed of 140 rpm (a further increase was not affecting the response of the silver electrode) and a 2-cm broad baffle. The reactants were introduced through two inlets, separated 2-cm from each other, and immersed into the solution down to 0.5-cm from the bottom of the vessel. Temperature, pH, silver potential, and addition rates were constantly screened. Silver electrode calibration curves were obtained for every solvent mixture in both clear solutions and in slurries containing silver bromide seed crystals.

Three main procedures were followed*:*

1. Nucleation periods: Stock solutions of $AgNO_3$ and KBr were introduced into a crystallizer containing 500 ml of a KBr solution in water or 5% ACN (acetonitrile) until precipitation of AgBr was observed. The maximum silver potential during nucleation and the time to be reached were measured at different experimental conditions (Table I). Temperature was 50°C.
2. Optimal procedure: The initial solution contained 5.77 g/L gelatin and 4.89-M KBr (pBr=1.31) in a volume of 433 mL. Stock solutions were: 1.96-M $AgNO_3$ and 1.96-

TABLE I. Comparison of the Solubility Products and Complex Formation Constants inProtic and Aprotic Solvents. Data taken from Ref. 8.

	Water		Methanol		Formamide	DMR		DMSO	
	pK_{so}	Logβ_2	pK_{so}	Logβ_2	pK_{so}	pK_{so}	Logβ_2	pK_{so}	Logβ_2
Cl	9.8	5.4	13.1	7.9	9.4	14.5	16.3	10.4	11.7
Br	12.3	7.6	15.2	10.6	11.4	15.0	16.6	10.6	11.4
I	16.0	11.2	18.3	14.8	14.5	15.8	17.8	11.4	12.5

M KBr. Nucleation was performed at 50°C, with a 12.2 mL/min addition rate for each reactant, for 28 s. Then, the temperature was raised to 70°C for 20 min and 9.5 g of gelatin in 95 mL of water were added. Crystal growth was performed with a silver flow rate of 1.5 mL/min for 4 min, which was constantly increased up to 7.5 mL/min for 76 min. The bromide flow rate was permanently regulated to maintain a silver potential of 18 mV.

3. Precipitation at critical conditions: The initial solution contained 5.77 g/L gelatin and 0.01-M KBr in a volume of 500 mL. Nucleation was performed at 50°C with reactant addition rates of 6 mL/min for 60 s. Then, the temperature was raised to 70°C for 20 min, and then, without any further addition of gelatin, growth was initiated. The silver addition rate during growth increased from 1.5 to 3.5 mL/min for 30 min with a constant gradient. The addition rate of the bromide stock solution was permanently adjusted to maintain the silver potential at the initial value. In this way the pBr remained constant all along the precipitation process and it had the same value in all the experiments.

Precipitation was performed in several media: pure water, 0.55-M KNO_3 solution, 1.0-M KNO_3 solution, and water mixtures containing respectively 5% of dimethyl sulfoxide (DMSO), 25% of DMSO, 20% of dimethyl formamide (DMF), 20% of acetone, 20% of ethanol, and 50% of ethanol. Stock solutions were prepared with pure water except in the case of ethanol experiments in which silver stock solution contained 33% ethanol. In 0.55- and 1.0-M KNO_3 experiments, initial solutions contained 0.005 mole/L extra of KBr in compensation for the diminution of the activity coefficient with ionic strength. Every experiment was performed at least twice.

Crystals were taken at several stages along precipitation and observed by optical microscopy. A population analysis was performed from EM pictures of carbon replicas of the samples accounting for side length and thickness of the crystals. Crystal size distribution was monitored by an electrochemical reduction analyzer. Fitting of the non-tabular crystal size distribution to a sum of two Gaussian functions was realized by using the Levenberg–Marquardt method. Several sets of trial values were used in every fitting and the method was always either converging to a unique solution or it led to incongruent values. Overall frequency and average size of the crystal populations were calculated from the EM pictures, the area of the fitted gaussian functions and the particle analyzer integration curve. The total number of crystals was calculated from the mean crystal volume and the total amount of solid precipitated. The average particle diameter after ripening was calculated from the total number of crystals and the amount of reactants added during nucleation. It was assumed that the number of crystals did not diminish drastically in the growth stage. Representative crystal samples were also observed by STEM (JEOL 1200EX) and TEM (JEOL 100C) equipped with a liquid nitrogen cooling holder.

Results

Nucleation Periods. The maximum silver potential reached during nucleation was measured for different concentrations of the stock solutions, different addition rates and in the presence of 5% ACN. The silver potential value is related to the concentration of free silver ion in the bulk of the solution. The resulting value was similar in all cases. However, the total amount of silver added to the solution when this potential was reached was different in each case (Table II). This amount was increased with the concentration of the stock solutions and in the presence of ACN and decreased with the pBr. Obviously, the extra amount of silver present in the solution at the moment of nucleation had to be in the form of silver halide complexes.

Precipitation at Optimal Conditions. Precipitation was carried out in solutions with an optimum pBr for the production of tabular crystals in the absence and presence of a 5% ACN (Fig. 3). Both the size and the aspect ratio of the tabular crystals obtained were considerably higher in the presence of ACN. The ratio of triangular-shaped crystals was also higher in this case (Table III). In addition, the ratio of small crystals decreased and the ratio of tetrahedral crystals increased in the presence of ACN. As a consequence, the crystal size distribution was narrower in the presence of ACN.

Precipitation at Critical Conditions for T-Grain Production. A pBr = 2.0 was chosen to elucidate the effect of the solvent on the production of tabular crystals (Fig. 4). Electron micrographs showed three main types of crystals. Crystals of the first type were small and spherical. Crystals of the second type were slightly larger and their shape was that of a truncated triangular bypyramide. The third included tabular crystals. Electron diffraction experiments showed that spherical crystals were single crystals while small triangular crystals and tabular crystals were {111} twins. STEM observations indicated that small triangular crystals had a unique twin plane parallel to the triangular faces. Other morphologies (tetrahedra, rods, etc.) were too rare to be classified, but, their volume was close to that of tabular crystals and they also contained twin planes. The particle size distribution analyzed by an electrochemical reduction technique showed two groups of crystals with a marked difference in size. The curve of the crystal size density of the group of small crystals showed two peaks that were clearly separated in some cases. This curve could be deconvoluted into two Gaussian functions (Fig. 5) with a small standard deviation. A comparison with the crystal size distribution obtained from the EM pictures showed that the first Gaussian corresponded with the population of small spherical crystals and the second with the little triangular crystal population. Generally, a certain deficit of density population in the smallest size ranges of the spherical population was probably the result of a ripening process during growth. The fact that the two populations of small crystals fitted well to a Gaussian size distribution showed that the three populations developed independently.

TABLE II. The Influence of ACN in the Nucleation Time and Silver Concentration During Nucleation

Solvent	*pBr*	*c* (×10^{-3}M)	*r* (ml/Min)	t_m (sec.)	[Ag_c] (×10^{-6}M)	[Ag_f] (×10^{-7}M)
Water	2	29.4	5	9	44.0	19.0
Water	2	2.94	5	23	12.0	22.0
Water	2	2.94	1	111	11.0	21.0
ACN 5%	2	2.94	1	195	19.0	20.0
Water	4	2.94	1	36	3.5	1.3
ACN 5%	4	2.94	1	102	10.0	1.6

TABLE III. Morphology and Size of Crystals Precipitated at pBr = 1.3, from EM Pictures

	Frequency (%)		Size (μm)		Thickness (μm)	
	Control	ACN5 %	Control	ACN 5%	Control	ACN 5%
Total counted	483	276				
Spherical	23.40	15.94	0.10	0.11	0.08	0.10
Triangular S1*	8.70	0.36	0.22	0.19	0.17	0.11
Triangular S2†	2.90	3.62	0.38	0.54	0.14	0.29
Tetrahedra‡	7.04	22.10	0.39	0.62	0.47	0.60
Tabular						
Total	54.24	55.43				
Hexagonal	22.52	9.15	0.73	1.08	0.11	0.14
Triangular	13.74	28.76	0.62	0.97	0.10	0.13
Hexa–tria	62.60	54.90	0.73	1.12	0.10	0.14
Trapezoidal	1.15	7.19	0.87	1.18	0.13	0.15

* Size smaller than 0.4μm.
† Size from 0.4 t0 0.9 μm.
‡ Most of the tetrahedra were truncated.

TABLE IV. Comparison of the Three Crystal Populations (pBr = 2.0)

	Population density				Projected area			
	Total (×10^{-11} cm^{-3})	Spherical (%)	Triangular (%)	Tabular (%)	Total (m^2)	Spherical (%)	Triangular (%)	Tabular (%)
Control	38	69	30	1.1	53	26	49	25
DMSO 5%	32	61	37	1.4	53	20	51	29
DMSO 25%	6	39	55	6.5	54	2	17	81
DMF 20%	24	55	43	2.0	66	16	38	47
Acetone 20%	16	52	46	1.3	63	7	44	49
Ethanol 20%	20	68	31	1.6	49	14	34	53
Ethanol 50%	2.3	20	76	4.2	52	0.5	10	89
I = 0.55 M	1.7	20	40	49.0	92	—	—	99

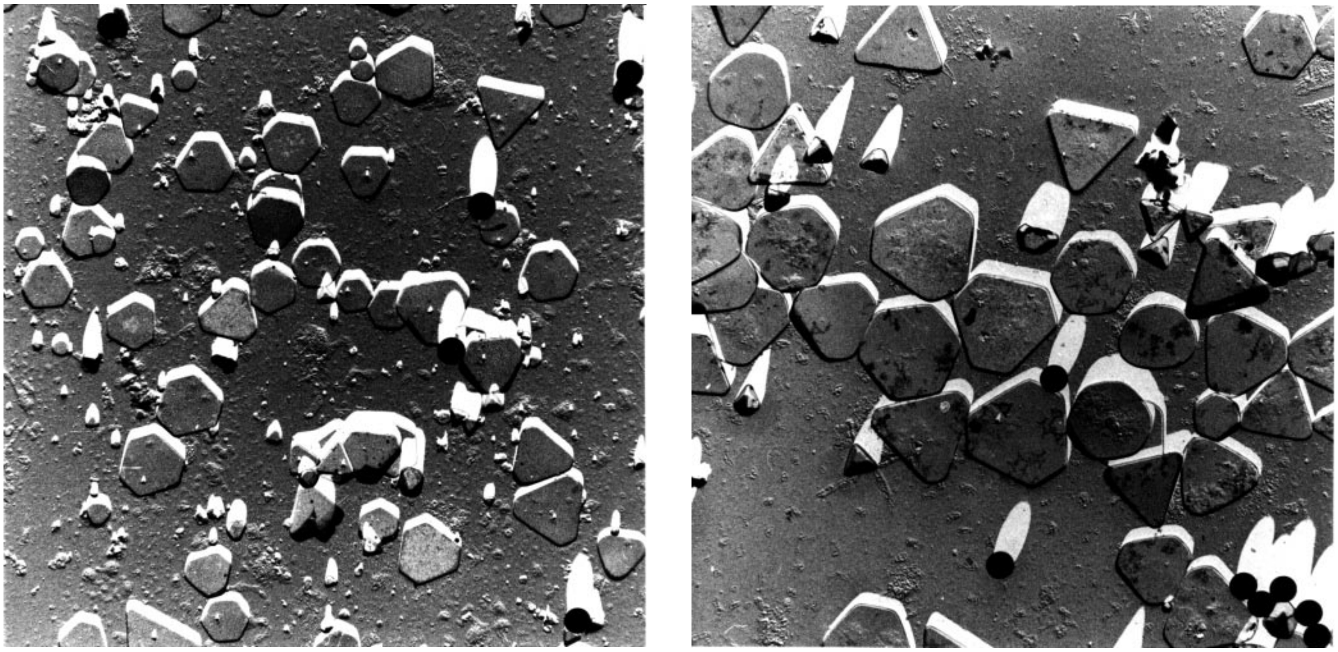
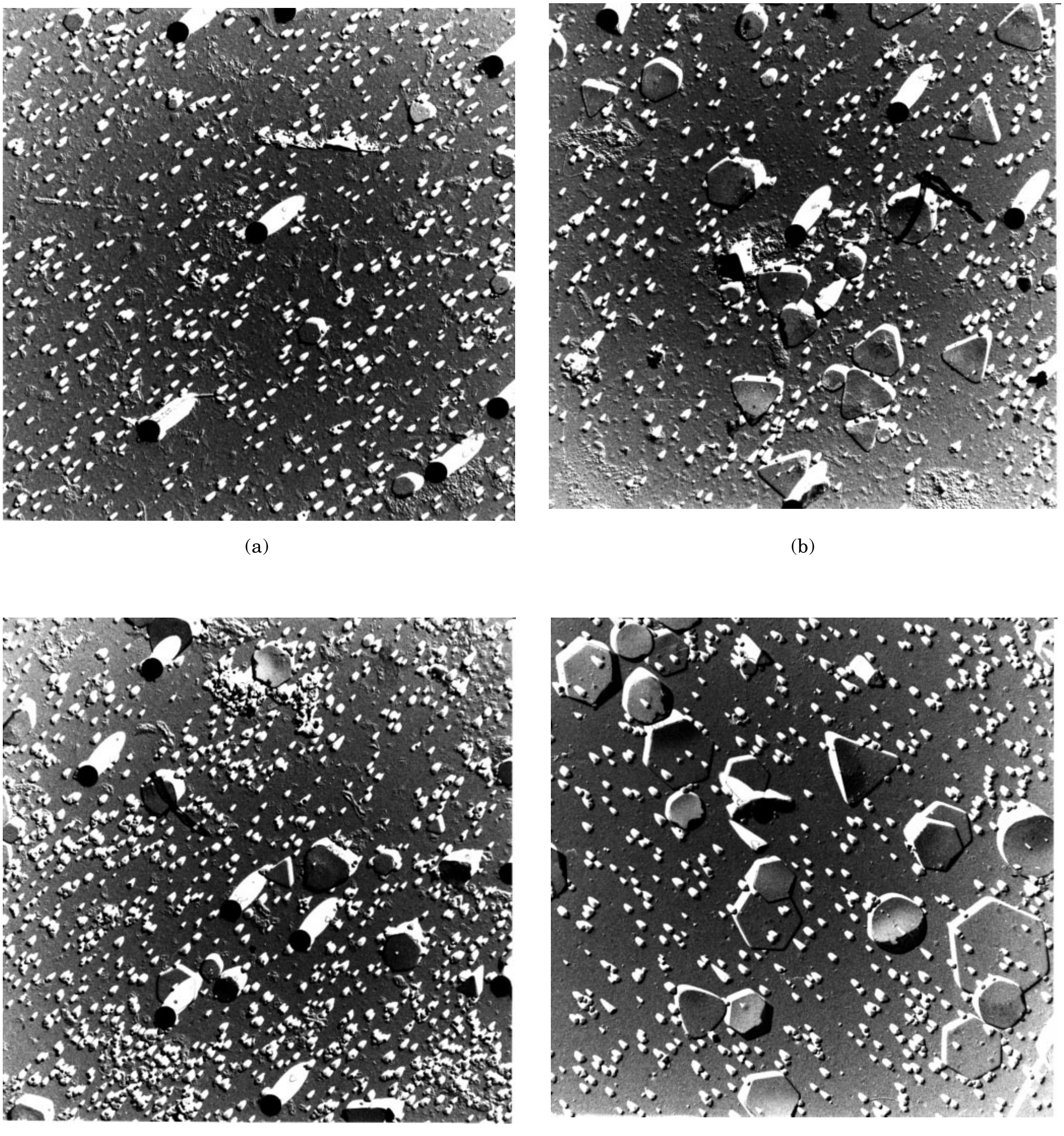


Figure 3. Carbon replica EM image of crystals precipitated at pBr = 1.3 in (a) pure water solutions, (b) 5% ACN solutions.



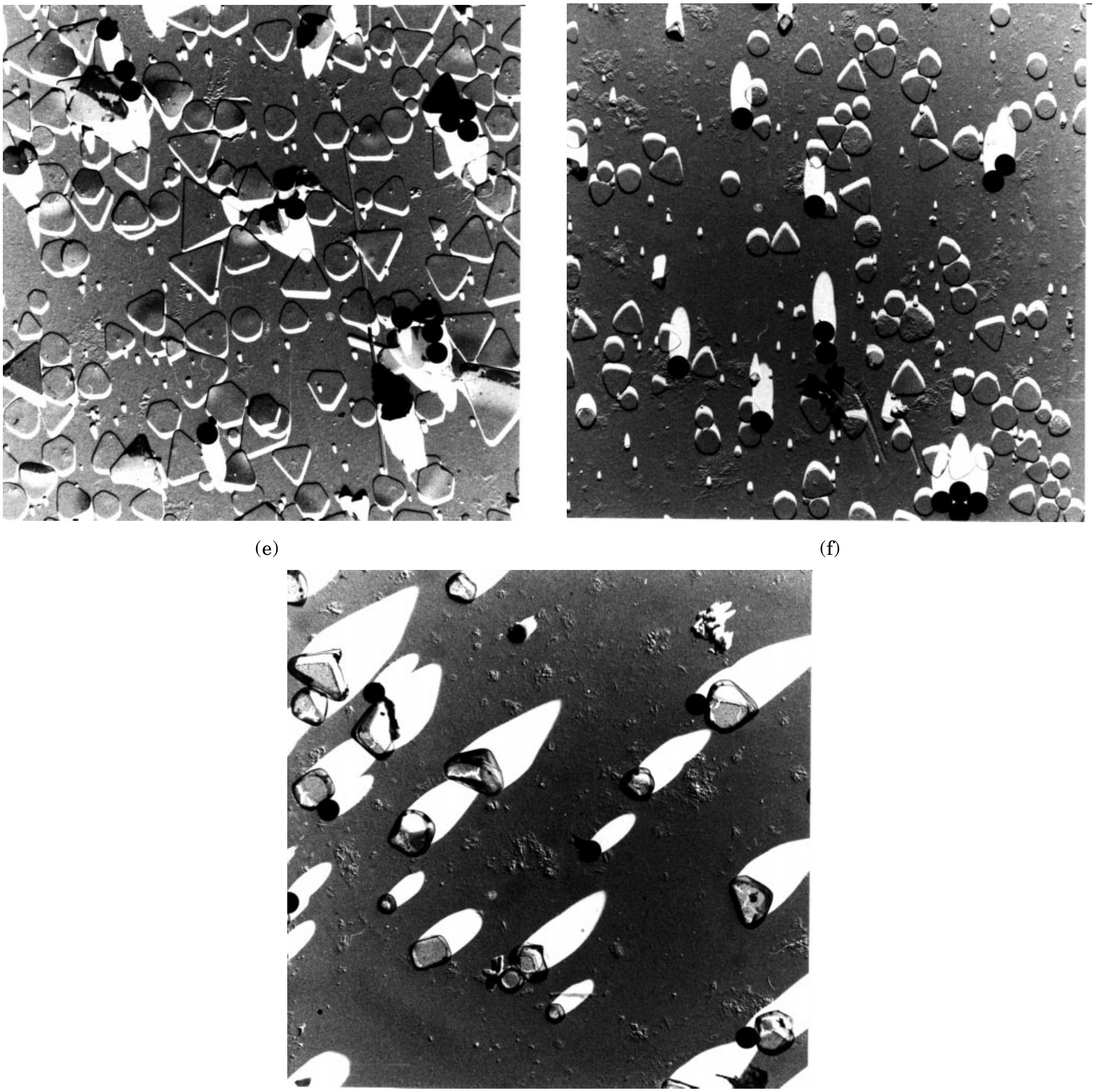
(a)

(b)

(c)

(d)

Figure 4. Carbon replica EM image of crystals precipitated at pBr = 2.0 in (a) pure water solutions, (b) 25% DMSO solutions, (c) 20% ethanol solutions, (d) 50% ethanol solutions, (continued page 390)



(e)

(f)

(g)

Figure 4 (con't). Carbon replica EM image of crystals precipitated at pBr = 2.0 in (e) I = 0.55 solutions, (f) I = 1.0 solutions, (g) AgCl crystals precipitated in 50% ethanol at pCl = 1.3.

TABLE V. Frequency and Size of Tabular Crystals in Several Media

	Frequency (%)			Side length (µm)			Thickness (µm)		
	Hexagons	Triangles	Hexa–tria	Hexagons	Triangles	Hexa–tria	Hexagons	Triangles	Hexa–tria
Control	66.0	14.0	20.0	0.39	0.90	0.66–0.38	0.11	0.10	0.10
DMSO 5%	68.5	5.5	26.0	0.39	0.75	0.69–0.42	0.09	0.10	0.08
DMSO 25%	54.5	31.5	14.0	0.63	1.97	1.28–0.61	0.09	0.09	0.09
Acetone 20%	60.0	8.0	32.0	0.71	2.46	1.20–0.81	0.09	0.09	0.08
DMF 20%	50.5	14.0	35.5	0.72	1.97	1.28–0.68	0.09	0.08	0.08
Ethanol 20%	52.0	12.0	36.0	0.63	1.37	0.92–0.56	0.07	0.08	0.07
Ethanol 50%	71.5	6.5	22.0	1.05	2.62	1.92–1.13	0.09	0.10	0.10
I = 0.55 M	24.0	23.0	53.0	0.65	1.89	1.10–0.51	0.06	0.07	0.06
I = 1.00 M	33.0*	15.5	51.5†	0.52	1.18	0.99–0.92	0.09	0.09	0.00

* Discs.

† Elipsoidal triangles.

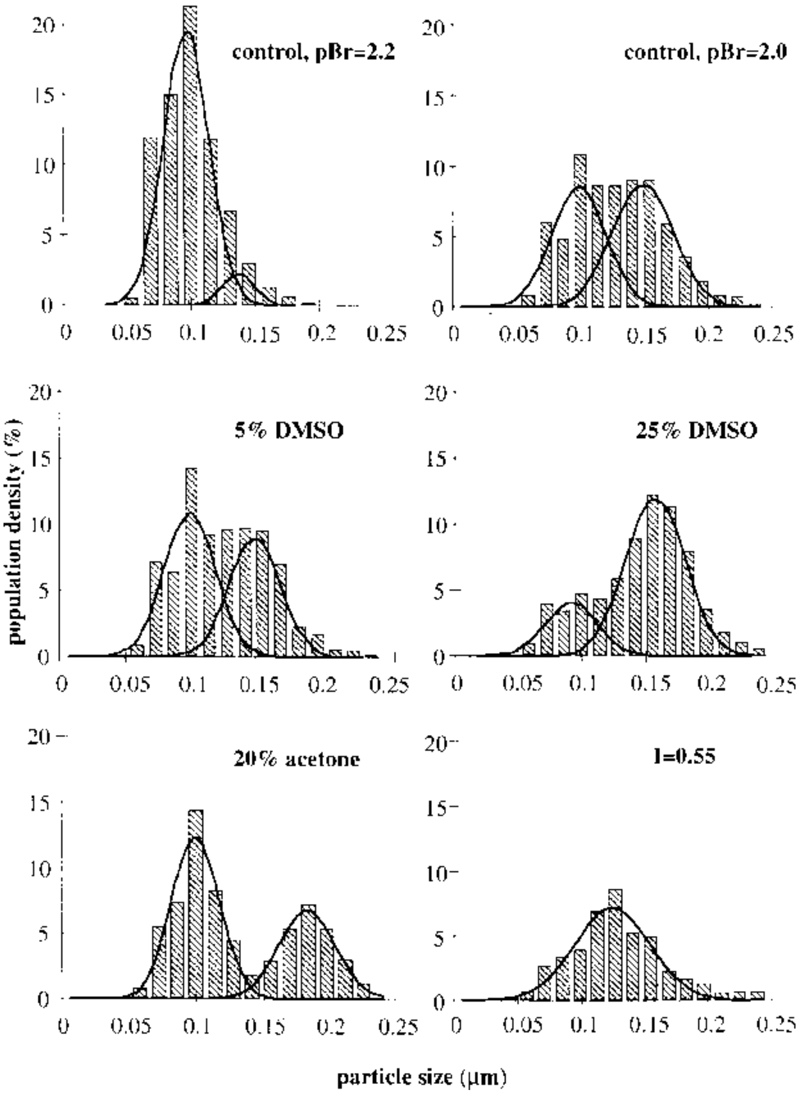


Figure 5. Fitting of Gaussian functions to a part of the crystal size distribution obtained from electrochemical reduction analyzer assigned to nontabular crystal population by comparison with EM pictures. That part corresponding to large sizes and assigned to tabular crystals is not represented in the plots.

Only 1% of the crystals was tabular in pure water solutions at pBr = 2. This ratio was increased in organic solvent mixtures, especially in the presence of DMSO. The highest ratio of tabular crystals in the precipitate was obtained in high-ionic-strength solutions (Table IV). In this media, spherical crystals were rarely present and triangular shape was dominant among tabular crystals (Table V).

The average crystal size after the ripening stage was about 0.02 μm. That is five times smaller than the average size of the spherical crystals at the end of the precipitation. That means that spherical crystals were also increasing their size during the growth stage. On the other hand, size and size distribution of spherical crystals were nearly the same in all the experiments. However, the size of the small triangular crystals was larger in precipitates from organic solvent mixtures than those from pure water solutions. In acetone and DMF media the population of triangular crystals was split off completely from that of spherical crystals (Fig. 5). The most significant effect of the organic solvents in the precipitate was a large increase of the size of tabular crystals. This crystal size enhancement was more relevant for acetone and DMF and it was proportional to the ratio of organic solvent in the media (compare 20% ethanol and 50% ethanol precipitates). Moreover, tabular crystal thickness was also slightly smaller in organic solvent precipitates. As a consequence, the aspect ratio of tabular crystals improved considerably in the presence of organic solvents. The enhancement of the tabularity of the emulsion produced by organic solvents can be well appreciated when looking at the ratio of the total projected area accounted for by the tabular population (Table IV).

Other more rare morphologies were observed like tetrahedra and, less often, rods, and thick trapezoids. As for tabular crystals, the frequency of tetrahedral crystals was low in the control sample, it increased in organic solvents, and it became significant in high-ionic-strength media.

Precipitation of silver chloride crystals in solvent mixtures was also tried. But many of the crystals were flattened and the tabularity of the emulsion was not high. The precipitate was composed of single twins bounded by {111} or {100} faces, cubes and cubo–octahedral crystals [Fig. 4]. In this case, the concentration of silver halide complexes in the solution did not come close to reaching the values obtained in silver bromide precipitation.

The use of organic solvents in the precipitating media in the double-jet method is limited by the solubility of gelatin in those media. For the concentrations of gelatin used in these experiments the maximum amount of organic solvent allowed in the media was about 50 to 70%.

Discussion

Three main populations of crystals were found in silver halide precipitates obtained by the double-jet method. The three populations were significant in number and experimented growth after ripening, at a pBr = 2. The first population, composed of crystals with a spherical shape, corresponds to single crystals. The second population, consisting of small crystals with a triangular shape, corresponds to single twins. And the third population, including large crystals with a tetrahedral, trapezoidal, or tabular shape, corresponds to multiple twins. The analysis of the crystal size distribution of the three populations showed that they developed independently. That means that there was hardly any conversion of crystals of one type into another type. Thus, small triangular crystals and tabular crystals originated during the nucleation or ripening stage.

The measured activity of free silver ions during nucleation was very similar in all the experimental conditions employed. But the amount of silver complexes increased with the concentration of the feeding solutions, addition rate of the reactants, and in the presence of organic solvents. In a parallel way, the ratio of tabular crystals in the precipitate also increased in those cases. It is evident that the enhancement of twin crystal nucleation goes together with an increment of the presence of silver complexes in the solution. Those silver complexes could have a direct participation in the formation of the twin nuclei as some authors have proposed.[6,7] But twinning could be the consequence of fast development of nuclei resulting from high availability of ions during nucleation. Then, silver complexes would not participate in the mechanism of twinning but they would just be a fast source of free silver ions for the growing crystal. This is connected to the theory stating that twinning is produced by high solubility.[20]

The growth rate of the three main crystal populations was influenced by the presence of organic solvents in several ways. The growth rate of un-twinned crystals was not affected. Single twin crystals (small triangular crystals) grew slightly larger. Tabular crystal growth rate was much increased in the lateral direction but slightly reduced in thickness. Thus, it is clear that polar aprotic solvents enhanced tabular growth. This phenomenon is probably based on the change of the solvating properties of the media in the presence of organic solvents. As discussed in previous sections, this change especially affects the halide ions present in high amounts in the media. It has been shown that aprotic solvents do not bind halide ions as stronger as water. This is clearly reflected on an increment of the presence of silver halide complexes in the solution. Considering that {111} surfaces are mainly composed of halide ions, their stability will also be enhanced in this way. Therefore, the rates for tabular growth founded in organic solvent solutions must be related to a larger presence of complexes in the solutions and higher stability of the tabular faces. Organic solvents may also affect the conformation of gelatin improving the availability of binding groups. In this way the effect of gelatin on the stability of {111} faces would be enhanced in the presence of organic solvents.

In high-ionic-strength solutions, the activity of complexes in the solution should not change with respect to pure water because the activities of free ions are the same. But the solubility would be increased and the stability of {111} faces reinforced by the effect of the large amount of foreign ions in the way discussed earlier here. Some authors suggested that twinning might take place by coalescence of particles.[22] In this mechanism, the presence of a high ionic strength would favor the occurrence of twinning events as found here.

The failure of organic solvents–water mixtures in producing silver chloride tabular crystals must be related to the strong binding of water molecules to chloride ions. The decrease of the capacity of the media to solvate chloride ions produced by the organic solvent was not enough to account for the stabilization of tabular faces.

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