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Conference Paper

Surface Reactions of Some Aqueous Silver Halide Dispersions*

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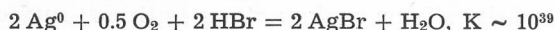
This review discusses interactions of cationic surfactants, cyanine dyes, gelatin, bromide ions and other Ag^+ -ligands with aqueous silver halide dispersions containing particles of controlled size, composition and crystal habit. Results are discussed in terms of adsorption energies and orientation of adsorbates; emphasis is placed on crystal habit as a variable both for adsorption equilibria and for kinetic processes like recrystallization (Ostwald ripening) and the dissolution rates of silver halide surfaces.

INTRODUCTION

As with many recent physical-chemical investigations of silver halides having photographic significance, the studies summarized here generally required suspended microcrystals of variable but known size, composition and crystal habit. Methods are available¹ for preparing such aqueous silver halide dispersions at high particle concentrations, and a number of techniques can be employed for the evaluation of their particle size and surface area. It will be shown that the resulting information can be applied to the characterization of kinetic phenomena such as silver halide dissolution rates by various Ag^+ -ligands or the recrystallization and Ostwald ripening of AgBr . Effects of silver halide composition in such reactions will be reviewed as will be the role of silver bromide cubic or octahedral crystal habit as a variable for the adsorption of bromide ions, cationic surfactants, cyanine dyes and gelatin.

SUBSTRATE PREPARATION AND CHARACTERIZATION

When in the course of these studies small-particle silver halide suspensions were needed that contained no gelatin or other polymeric vehicle, it was convenient to use ca. 10 nm Ag^0 sols because such silver particles can be partly or completely converted to silver halide dispersions², e. g.,



More generally, however, silver halide dispersions were prepared from highly water-soluble salts in dilute gelatin solution by a double-jet homogeneous nucleation process¹. This technique can facilitate formation of AgX suspensions having controlled particle sizes because of a correlation between

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the silver halide's equilibrium solubility, a thermodynamic parameter, and the kinetics of silver halide particle growth. Evidence for the existence of such a correlation is given in Figure 1; it shows that the size of AgI crystals formed as a function of pAg paralleled AgI solubility in the same pAg range³. Similarly, parallel changes of AgBr solubility and its rate of Ostwald ripening were reported over a wide pAg range⁴.

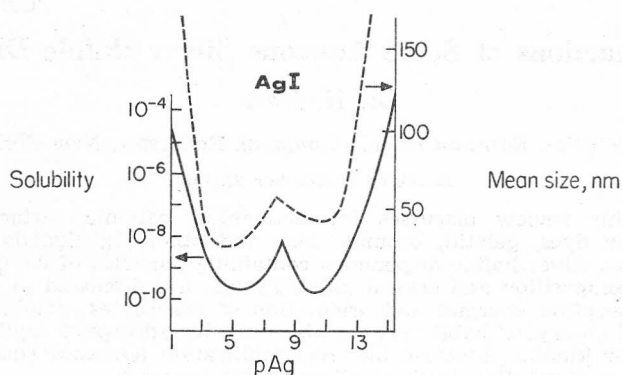


Figure 1. Relation between AgI solubility and particle size in aqueous dispersions. The equilibrium solubility near 20 °C is given in mol l⁻¹ H₂O; the plotted mean crystal size relates to particles obtained by precipitating AgI at the indicated pAg in aqueous gelatin at 35 °C.

Although electron microscopy is frequently used for characterizing the size and dispersity of silver halide suspensions, particle dimensions were also obtained by other techniques that included Rayleigh scatter⁵⁻⁷, the Coulter Counter and dye adsorption^{8,9}. For the latter purpose, 1,1'-diethyl-2,2'-cyanine was preferred because various workers are in reasonable agreement that this dye occupies a limiting area per molecule of ca. 0.58 nm² at aqueous AgCl, AgBr and AgBr/I surfaces^{9,10}. This limiting surface occupancy by the cyanine did not vary with the substrate's crystal habit. Moreover, in a useful concentration range, this dye existed primarily in either its dissolved and unperturbed form or in its adsorbed state that exhibited the distinct and intense long-wavelength absorption of a J-aggregate. Monitoring these spectral features by transmission or reflectance spectrophotometry without any intervening phase separation procedures allowed the convenient determination of dye surface coverages and, hence, the surface areas of silver halide dispersions^{7,9}.

Although gelatin had no apparent influence on the saturation coverage by that 2,2'-cyanine^{11c}, there is evidence that this polyelectrolyte may alter the orientation of fatty tail cationic surfactants at AgBr/Br⁻ surfaces. At any rate, since most silver halides discussed here contain ossein gelatin with an isoionic point (IP) at pH ~ 4.9, it should be recognized that this protein appears to be bound to both cubic and octahedral AgBr surfaces by only a few of its polar groups and that the remainder of the molecule extends some 20–40 nm into solution in highly solvated loops^{11a,b}. In weight terms, 3–8 mg gelatin/m² is irreversibly adsorbed to AgBr/Br⁻ surfaces, the maximum amount being adsorbed at the IP where gelatin exists as a random coil rather than in an extended configuration^{11b,c}.

This measured thickness of adsorbed gelatin indicates that chains of this polyelectrolyte extend much further into the aqueous solution than was calculated for the electrical double layer due to bound lattice ions at the silver halide surface. Hence, electrokinetic properties of AgX dispersions in the presence of gelatin are insensitive to excess lattice ions (pAg) but vary with the pH-dependent charges of the protein^{1a,12,13}.

SURFACE EFFECTS OF AgX DISSOLUTION RATES

Because of its practical importance, many studies have been concerned with fixing, i. e., the conversion of a sparingly soluble, dispersed silver halide to a highly soluble and removable Ag⁺-complex such as an argentothiosulfate¹⁴. These studies often employed clearing rates involving the complete dissolution of the AgX crystals by the Ag⁺-ligand. In order to separate this bulk behavior from reactions of the ligand at the AgX/solution interface, an electrochemical procedure was used that monitored the initial formation of Ag⁺-ligand complexes in the silver halide dispersion¹⁵.

More specifically, experiments were carried out with silver halides dispersed in alkaline gelatin solutions at constant ionic strength and temperature. In the presence of excess ligands such as ethanolamines or sulfite, the initial dissolution rates, r_i , were insensitive to the crystal habit of AgBr but they increased in direct proportion to (1) the effective surface area, A , of the silver halide, (2) its apparent solubility product, K_{sp} , and (3) for ligands of equal charge, the product of the total ligand concentration squared, L_0^2 , and the stability constant of its Ag⁺ complex, β_2 .

The results¹⁵, some of which are illustrated in Figure 2, made it apparent that $r_i = a(A\beta_2L_0^2K_{sp})$, where a depends on factors such as the concentration

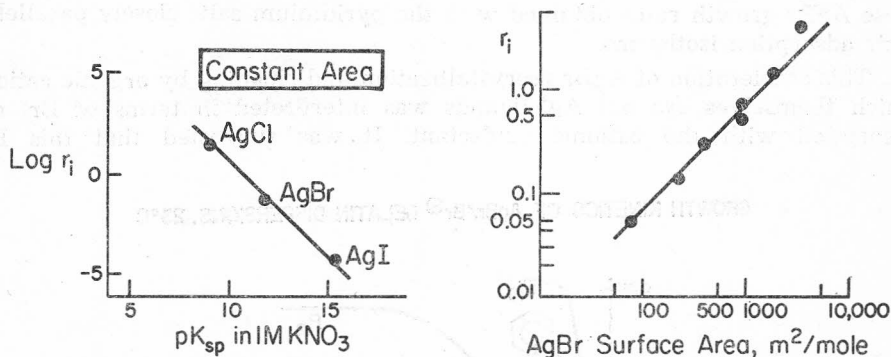


Figure 2. Initial silver halide dissolution rates (r_i) in 0.2 M Na_2SO_3 . The silver salts were dispersed in 0.5% aqueous gelatin near pH = 11, and the given data illustrate effects on these rates by variation of silver halide composition and solubility product at constant surface area as well as changes of surface area at constant AgBr composition¹⁵.

of excess halide (pAg) and ligand charge. This charge-dependent factor was particularly important; a decreased more than tenfold when an anionic group was introduced into an alkylamine¹⁵. However, this retardation could be avoided by the presence of reversibly adsorbed cationic surfactants which are known to diminish the negative charge density at silver halide/halide surfaces^{8,12}. These observations were interpreted by use of a model involving the formation

of charged Ag^+ -complexes at the charged $\text{AgX}/\text{solution}$ interface and a rate-determining process whereby the complexed Ag^+ diffuses from the AgX surface into the bulk of the solution¹⁵.

RELATIONS BETWEEN SILVER HALIDE SURFACE STABILITY AND ADSORPTION OF ORGANIC CATIONS

The properties of many silver halide/surfactant systems were recently reviewed¹³; they made it apparent that *N*-alkyl pyridinium and quinolinium salts are good examples of the just cited cationic surfactants which can diminish or reverse the negative charge of AgX/X^- suspensions. More specifically, it was demonstrated in AgBr and AgBr/I dispersions containing excess halide that the reversible Langmuir adsorption of these colorless organic cations increased with the length of their alkyl chain and yielded free energies of adsorption which ranged up to 11 kcal/mol. Adsorption parameters were insensitive to changes of silver halide composition or crystal habit, but for cations with 12 or more methylene groups, the limiting area/cation became independent of alkyl chain length. The resulting molecular areas were consistent with a surfactant orientation such that its cationic head was bound to the silver halide and the alkyl chain turned towards the gelatin solution⁸.

During these adsorption determinations, it was unexpectedly observed that the cationic surfactants destabilized silver halide/halide surfaces, e. g., *N*-dodecyl pyridinium pts (P_{12}) caused well-defined cubic AgBr to recrystallize to spherical particles^{7b}. This recrystallization was evaluated quantitatively with Rayleigh scatter in the presence of surfactants having various structures and concentrations. It was thus established that the Ostwald ripening rate of silver bromide at pBr 3 exhibited the concentration dependence for added *N*-alkyl pyridinium salts illustrated in Figure 3. It also became apparent that these AgBr growth rates obtained with the pyridinium salts closely paralleled their adsorption isotherms.

This acceleration of AgBr recrystallization and ripening by organic cations which themselves are not Ag^+ -ligands was interpreted in terms of Br^- co-adsorption with the cationic surfactant. It was suggested that this Br^-

GROWTH KINETICS OF $\text{AgBr}/\text{Br}^\ominus$ GELATIN DISPERSIONS, 23°C

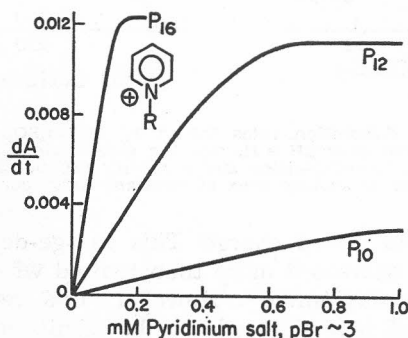


Figure 3. Growth kinetics (dA/dt) of AgBr/Br^- in aqueous gelatin at various concentrations of decyl, dodecyl and hexadecyl pyridinium salts^{7b}.

counterion adsorption, which was independently determined⁸, sufficiently enriched the Br^- concentration in the electrical double layer to facilitate formation of mobile silver bromide/bromide complexes, e.g., AgBr_2^- , which are known to accelerate AgBr recrystallization^{7b}.

Unlike the cited pyridinium or quinolinium surfactants, cationic cyanine dyes (and differently charged analogs) tend to stabilize silver halide surfaces against recrystallization because they are irreversibly adsorbed⁸. It appears that any anionic silver complexes that are formed in association with the irreversibly bound dye cation are also immobilized and thus they cannot participate in the silver halide recrystallization process^{7b}.

DOES THE CRYSTAL HABIT OF SILVER HALIDE INFLUENCE SURFACE REACTIONS?

The answer to this question would be negative if we were to base all conclusions only on the just-cited observations. These showed that in sulfite solution both cubic and octahedral AgBr surfaces dissolved at similar initial rates and, furthermore, that the adsorption properties of gelatin and of simple cationic surfactants were insensitive to AgBr crystal habit.

However, a different answer emerges when consideration is given to the interaction of cyanine dyes and of bromide ions with cubic and octahedral AgBr surfaces. Although the zero-point of charge of AgBr dispersions¹² and their thermodynamic constants for Br^- adsorption are not sensitive to the substrate's crystal habit, nearly twice as much Br^- is associated with octahedral than with cubic surfaces (Table). This dependence of Br^- coverage on AgBr

TABLE
*Bromide Ion Adsorption at Crystallographically Defined
AgBr Surfaces in Aqueous Gelatin at pH = 4.9, 40 °C^{16a}*

AgBr Crystal Habit	ΔG kcal/mole Br^-	ΔH kcal/mole Br^-	ΔS cal/deg/mole Br^-	Limiting Area/ Br^- nm^2
Cubic	-5.9 ± 0.1	-10.7 ± 0.4	-15	1.21
Octahedral	-6.2 ± 0.1	-11.5 ± 0.4	-17	0.80

crystal habit is reproducible^{12,17} and suggests that anions such as thiocyanate, or certain nitrogen acids having an affinity for Ag^+ similar to that of Br^- , should also exhibit a dependence of surface coverage on AgBr crystal habit¹³. Moreover, the present results demonstrate that only a small fraction of the geometrically available AgBr/solution interface is involved in Br^- adsorption at lattice sites.

As recently summarized, the situation for dye adsorption is different¹⁶. Many cyanines are strongly bound to the AgX surface in a close-packed array, and it was demonstrated that a reversibly adsorbed anionic thiocarbocyanine yielded free energies, enthalpies, and entropies of adsorption that were essentially identical for both cubic and octahedral AgBr^{16a}. Furthermore, this dye and its analogs exhibited limiting areas per adsorbed molecule that were the same for both AgBr types, yet the dye's surface spectra clearly and strikingly varied with the substrate's crystal habit^{9b,16,18}. This dye behavior remains poorly understood, and investigations are continuing to determine how the orientation and stacking of dye molecules is controlled by the crystallographic index of silver halide surfaces.

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SAŽETAK

Površinske reakcije vodenih disperzija srebrnih halida

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Prikazani su rezultati istraživanja interakcija kationskih površinski aktivnih tvari, cijaninskih boja, želatine, bromidnih iona i drugih liganada srebrnog iona s disperzijama srebrnih halida kontrolirane veličine čestica, sastava i kristalnog habitusa. Pretpostavivši da je kristalni habitus osnovna varijabla i za adsorpciju i za kinetičke procese rekristalizacije (Oswaldova sazrijevanja) i otapanja, rezultati su diskutirani s obzirom na slobodnu energiju, entalpiju i entropiju adsorpcije bromidnih iona, te orijentacije adsorbata na kubičnom i oktaedralnom AgBr.

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