

On Silver Iodide in Surfactant Solutions*

R. Despotović and D. Mayer

Laboratory of Colloid Chemistry, »Ruđer Bošković« Institute, 41001 Zagreb,
P. O. Box 1016, Croatia, Yugoslavia

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The role of *n*-dodecylammonium nitrate, DDANO₃, at the interface (AgI)_{solid}/(electrolyte)_{solution} was investigated. Silver iodide was prepared (i) by isoelectric precipitation, (ii) by equivalent precipitation in *statu nascendi*, and (iii) in an excess of potassium iodide in the presence of DDANO₃. The employed surfactant affects the crystallographic and colloid properties of AgI in various ways. The influence of surfactant was examined in the course of precipitation and peptization of silver iodide. Based on the results obtained, a mechanism of the interaction of silver iodide sols with surfactants was suggested. The proposed model indicates the role of surfactant in the equilibration process at the interface »crystal/electrolyte solution« in the processes of the solid phase formation and peptization.

INTRODUCTION

In a series of previous investigations the dependence of the properties of colloid silver iodide suspensions on the concentration and chemical nature of cationic, non-ionic, and anionic surfactants present was shown¹⁻³. In all examined cases the surfactants were present in systems in *statu nascendi*, that is, at the beginning of suspension formation. Suspensions change during aging and the analysis of results shows, that at higher surfactant concentrations a multi-component system »silver iodide with surfactant bound on the crystallite surface + silver iodide surrounded by precipitated surfactant + precipitated surfactant« is formed⁴. After a certain time the entire system reaches equilibrium in which the silver iodide particles settle down. Mechanisms of sedimentation were considered in the light of Van der Waals attractive forces, stereochemical factors, and electrostatic interaction between charged particles and surfactant ions^{1,4,5}. The radiometric investigation of the substructure transformation through the precipitation process reveals a number of simultaneous processes in the stable silver iodide sols; the embryos disappear transforming into the solid phase, the silver iodide particles grow and the remained metaphasic silver iodide disappears turning into the solid phase⁶. By following an inversion process *i. e.* the formation of a stable dispersion from flocs or sedimented particles reversibility of assumed sedimentation mechanisms could be verified. In order to determine the flocculation-peptization reversible processes, the peptization of silver iodide was investigated under different

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conditions. The results obtained show interesting relations between both phenomena; flocculation and peptization at similar concentrations of the same surfactant present in the systems.

EXPERIMENTAL

Analar grade BDH sodium iodide and silver nitrate were used, and solutions were prepared and standardized by the usual procedure. *n*-Dodecylammonium nitrate DDANO₃ was prepared by dissolving *puriss* grade Fluka *n*-dodecylamine in 1:1 nitric acid. In this way so prepared DDANO₃ was purified by five recrystallization and filtration from hot 50% ethanol containing charcoal (p. a. Merck, Darmstadt). Isoelectric silver iodide AgI_E was prepared by adding a 0.02 M AgNO₃ solution into an equal volume of 0.02 M NaI until a paraffined Ag/AgI electrode indicated a pAg value of 5.2–5.6. The precipitate, aged for 100 minutes, was filtered and washed until the washings showed constant conductivity. The AgI_E precipitate was kept in water. 0.53 g of AgI_E weighed in water by the Mohr-Westphal balance was put into contact with various concentrations of 200 ml DDANO₃ solutions containing 0.10 M NaI. After 60 minutes of ageing in the surfactant solution, 100 ml of the suspension were pipetted off to which a 0.5 ml saturated Mg-nitrate solution was added. The suspension was left to stand for 1000 minutes, and silver iodide was filtered, washed, dried and weighed afterwards.

The silver iodide AgI_E was prepared by equivalent precipitation *i. e.* by adding a 0.01 M AgNO₃ solution to an equal volume of 0.10 M KI containing various concentrations of DDANO₃. After 1000, 10000, and 100000 minutes of ageing the supernatant solutions of the suspensions were separated by centrifuge and the concentrated AgI sols were transferred into a sample holder for X-ray diffractometry. The crystal modification (percent of hexagonal AgI_E, H%) and crystallite sizes R_{H(100)} of hexagonal silver iodide were determined by recording 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.

RESULTS AND DISCUSSION

X-ray diffraction analysis showed a complex dependence of the cubic/hexagonal ratio and the crystallite sizes on chemical conditions⁷. Colloid characteristics follow crystallographic and the crystallite size changes. Contrary to the conventional opinion that surfactants hinder the Ostwald's ripening process a number of X-ray data show that in the presence of surfactants the crystallographic and dispersity changes could be accelerated or hindered^{2-4,7}.

Early investigations have shown that in the absence of surfactants the precipitation from equivalent solutions yield approximately equal fractions of cubic and hexagonal silver iodide⁸. With concentration ranges of surfactant DDANO₃ from 0.000002 M to 0.0003 M concentrations from the critical flocculation concentration to the critical stabilization concentrations are covered. Since aging is also one of the relevant factors all the systems under examination were aged for 1000, 10000, and 100000 minutes in the supernatant solution. In systems containing 0.00005 M DDANO₃ only 27 per cent of hexagonal silver iodide was obtained (Figure 1.A), while at higher or lower DDANO₃ concentrations a greater percentage of hexagonal silver iodide was formed. During aging the fraction of cubic silver iodide decreases, while in the systems with sodium dodecyl sulphate the fraction of the hexagonal modification decreases by aging². The Ostwald's ripening process was measured in all systems with DDANO₃ except in the case of 0.00005 M DDANO₃ (Figure 1.B). According to the zero point of electrophoretic mobility⁸ at which the particle surface of silver iodide is surrounded by the DDANO₃ surfactant, crystal growth is markedly hindered *i. e.* the connection between the crystal surface

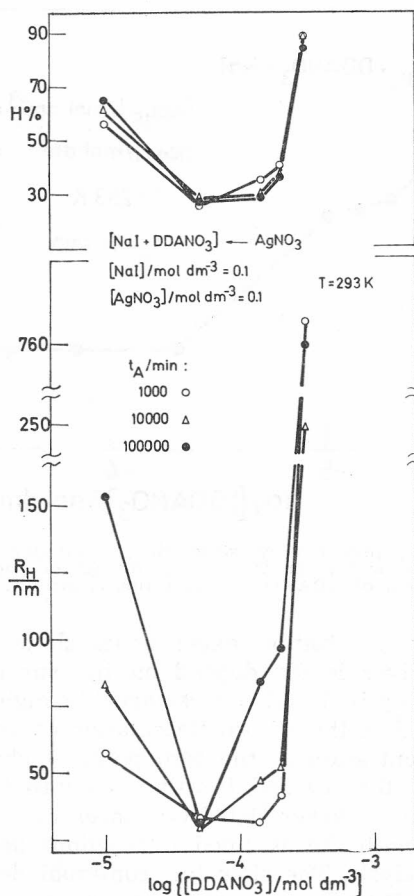


Figure 1. Silver iodide AgI_E prepared by equivalent precipitation was aged for $t_m = 1000$, 10000, and 100000 minutes in the supernatant containing the surfactant *n*-dodecylammonium nitrate, DDANO₃. The percentage $H\%$ of the hexagonal silver iodide (Figure 1.A) and the average crystallite size $R_{H(100)}$ (nm) were plotted (Figure 1.B) as a function of surfactant concentration (log scale) at 293 K.

and surrounding solution is markedly diminished⁴. At lower DDANO₃ concentrations, contrary to the conventional opinion, crystal growth is faster in the presence of the surfactant as compared with similar systems without surfactants⁶. Results are in agreement with the hypothesis of the negative charge barrier surrounding the primary colloid particles^{6,10}. Electrically positive DDANO₃ ions bound to the negatively charged particle at the crystal surface, on selected sites¹¹. Uncovered particle surface is open to contact with the surrounding solution. In the case of high surfactant concentrations silver iodide particles are not closely accumulated because surfactant micelles are accumulated between crystal planes¹. In this way crystallite surfaces are open for the ripening process, and as a consequence, crystallites grow during the aging of the suspension. In the light of such considerations the minimum value of $H\%$ can be explained.

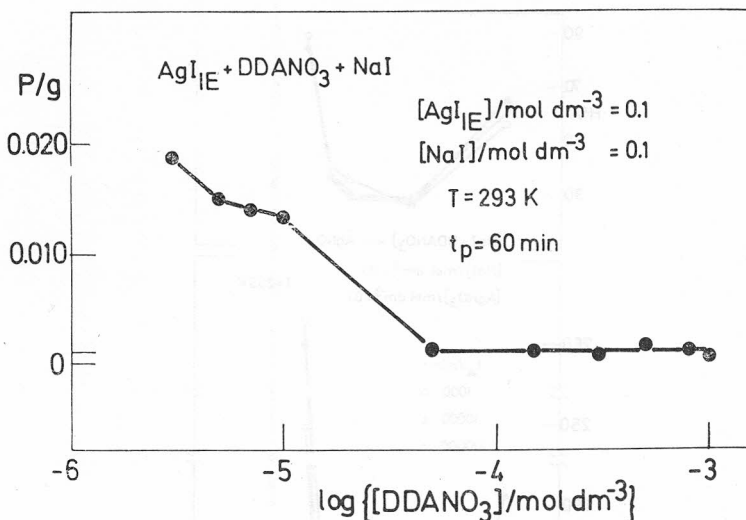


Figure 2. Silver iodide AgI_{IE} prepared by isoelectric precipitation was aged in 0.10 M NaI solution for $t_m = 60$ minutes, and amounts of P grams (g) of peptized silver iodide were measured as a function of DDANO_3 concentration present in the NaI solution.

The results of the peptization experiments show (Figure 2.) that the amounts of peptized silver iodide depend on the surfactant concentrations. The amounts P (g) of peptized AgI are remarkably higher at surfactant concentrations which are below the critical flocculation concentration of DDANO_3 . For the DDANO_3 concentration at the zero point of charge ($c_{\text{zpc}} = 0.00017 \pm \pm 0.00006$ M DDANO_3)⁴ the reached P value is approximately by one order of magnitude lower than at lower DDANO_3 concentrations. The results are in quite good agreement with the assumed interactions described in the X-ray diffractometry data analysis. The slow but continual decrease of obtained P values with increasing DDANO_3 concentrations is a consequence of the coverage of the AgI crystallite particles since the formed and agglomerated silver iodide was put into contact with DDANO_3 . The coincidence between the obtained results in two opposite ways confirm the assumption about the interactions between surfactant ions and silver iodide particles.

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SAŽETAK

O srebrnom jodidu u otopinama tenzida

R. Despotović i D. Mayer

Istraživan je utjecaj tenzida *n*-dodecilamin-nitrata DDANO₃ na granicu faza u sistemu »(AgI)_{čvrsto}/(elektrolit)_{otopina}«. Srebrni jodid pripremljen je (i) izoelektričnim taloženjem, (ii) ekvivalentnim taloženjem 'in statu nascendi' i (iii) uz suvišak kalijevog jodida u prisustvu DDANO₃. Primijenjeni tenzid utječe na kristalografska i koloidna svojstva srebrnog jodida na različite načine. Utjecaj tenzida ispitivan je u toku taloženja i u toku peptizacije AgI. Na temelju dobivenih rezultata izveden je zaključak o mehanizmu međudjelovanja između sola srebrnog jodida i tenzida. Izveden je model procesa uravnotežavanja međudjelovanja u granici »kristal/elektrolitna otopina« u procesima nastajanja čvrste faze i u toku peptizacije.

INSTITUT »RUĐER BOŠKOVIĆ«
41001 ZAGREB

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