On Negative Silver Iodide Sols in Sodium \( n \)-Laurylate Solutions

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This paper describes a physico-chemical study of the interaction between the anionic surfactant sodium \( n \)-laurylate NaL and the negative stable silver iodide prepared \( \text{in statu nascendi} \), with emphasis on the colloid properties of the system in aqueous media. Negative stable silver iodide sols of 0.001 M contained NaL solutions from 0.0000001 M to 0.01 M with 0.001 M NaI at 20 °C. Turbidity measurements show the formation of two pronounced Tyndall maxima; electron microscopy and X-ray diffraction analysis data show the dependence of crystallite sizes and sol densities on the concentration of NaL. For the systems examined under ageing the results obtained indicate, as a reasonable possibility, that different effects of NaL on negative silver iodide sol \( \text{in statu nascendi} \) for systems with NaL below and above the critical micellar concentration can be proposed.

INTRODUCTION

The effects of surface active substances or surfactants on colloid stability of silver iodide sols have been studied by many authors and the results obtained show that ionic type surfactants act like inorganic ions even at very low concentrations. As a rule the majority of published results are concerned with the explanation of interactions between silver halide colloids with surfactant ions of opposite electric charge, but rarely with nonionic surfactants\(^1\). Since the coagulation, as one of the most important colloid processes, caused by inorganic ions is different from the flocculation by surfactants, it is of special interest to study the influence of anionic-type surfactants on the behaviour and properties of negative sols or the influence of cationic-type surfactants on positive sols. Some published data on examinations of negative silver iodide suspensions in solutions of anionic surfactants show that the properties and behaviour of negative silver iodide sols are dependent on the concentration of the anionic surfactant present in the system\(^4\). Following these facts (i) turbidity, (ii), electron microscopy, (iii) X-ray analysis, (iii) microelectrophoresis, (v) resistivity, (vi) tensometry and (vii) radiometry measurements were applied in the attempt to explain the mechanisms determining the interactions of an anionic surfactant with negative silver iodide sols.

EXPERIMENTAL

Materials

Puriss. grade Fluka AG. Buchs SG \( n \)-dodecanoic acid was dissolved in ethanol: water 1:1 containing p. a. grade Merck (Darmstadt) sodium hydroxide. The sodium \( n \)-dodecanate NaL thus prepared was purified by five recrystallizations and fil-
tration from hot 50% ethanol containing active carbon (p. a. Merck, Darmstadt). The recrystallized NaL was dried under vacuum and stored in a desiccator. The water used in preparing NaL solutions was doubly distilled in an all glass Zellner apparatus (Jena-Schott). Analar grade B.D.H. sodium iodide, NaI, and silver nitrate, AgNO₃, were used for the preparation of standard solutions.

Turbidity

The measurements of Tyndall values T.V. were performed with a Pulfrich photometer with a turbidimetric extension (Carl Zeiss, Jena). The silver iodide sols were prepared by adding a 0.002 M silver nitrate solution to an equal volume of a 0.004 M sodium iodide solution containing varying concentrations of NaL so that a silver iodide sol was obtained with AgI 0.001 mol/l, pI = 3 (pI = -log c₁⁻), pH = 10 (adjusted by adding conc. NaOH) and 0.0000001 M to 0.01 M NaL. Before determining the T. V. the systems were allowed to age for tₐ = 10 to 10000 minutes at 20°C. The results are collected in Figures 1. and 2.

Electron Microscopy

The AgI sols in statu nascendi (AgI 0.001 M, NaI 0.001 M, cNaL 0.00001, 0.0001, 0.0005, 0.001 and/or 0.008 M) aged for tₐ = 100 minutes were taken for electron-micrography. Electron microscopy was carried out using a Trüb-Tauber Co. (Zürich) KM-4 electron microscope. Mowital films were used for supporting the specimens under examination. The results of turbidity and electron microscopy for 100 minutes aged systems are summarized in Figure 2.

X-Ray Analysis

The crystallite size was determined with a Philips diffractometer and evaluated according to Scherrer’s formulae using the angular line widths at half of the maximum
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Figure 2. Systems: Silver iodide sols prepared «in statu nascendi» (AgI 0.001 mol/l) at 0.001 M NaI, T = 20 °C, concentration of sodium n-laurylate c(M) NaL = var. Electron micrographs of silver iodide samples prepared at 0.00001 M, 0.0001 M, 0.0005 M, 0.001 M, and 0.008 M NaL. Open circles data and full curve correspond to T. V. values measured as a function of NaL concentration.

intensity. The particle sizes were determined on silver iodide sols in contact with the original supernatant liquid. Stable sols were concentrated with a superspeed Sorvall centrifuge RC2B. The particle sizes in systems aged for 100 minutes are plotted vs. NaL concentration in Figure 3.

Microelectrophoresis
The particle charge and the electrophoretic mobility \( \mu \) (cm\(^2\) s\(^{-1}\) V\(^{-1}\)) of the suspensions, which were prepared in the same way as for turbidity measurements, were determined by ultramicroscopic microelectrophoresis of silver iodide sols aged for 100 minutes and containing various concentrations of NaL. The results are summarized in Figure 3.

Resistivity Measurements
Resistivity \( R \) (Ω cm) of the NaL solutions was determined by means of a Cambridge high frequency conductometer using a conductivity cell with normal platinum electrodes. The results are shown in Figure 4.

Tensometry
The surface tension \( \sigma \) (dyn/cm) of NaL and NaL + NaI solutions was determined by means of a Lecomte du Noyé torsion balance (semiautomatic type, Krüss, Hamburg). The average results of 7 measurements are presented in Figure 5.

Radiometry
Sodium iodide solutions containing NaL were labelled with carrier free radio-iodine \(^{131}\)I before precipitation. The silver iodide sols were prepared in statu nascendi. The fractions \( f_S \) of »free« silver iodide can be derived as \( f_S = (A_S - A_I)/(A_I) \); after 100
Figure 3. Systems: Silver iodide sols prepared "in situ nascentie" (AgI 0.001 mol/l) at 0.001 M NaI, T = 20 °C, concentration of sodium n-laurylate c(M) NaL = var. Electrophoretic mobility \( \omega \) (cm²/s/V), crystallite size \( R(A) \) of AgI and Tyndall values T.V. are plotted against NaL concentration.

Figure 4. System: Sodium n-laurylate NaL dissolved in water. Resistivity \( R(\Omega \text{ cm}) \) is plotted against NaL concentration (square root scale). The tangent intersection indicates the critical concentration for micelle formation \( c_M \).
minutes of ageing an aliquot of the homogenized suspension was used for determining $A_0$ radioactivity; an equal volume of clear supernatant (after centrifugation) was counted as $A_i$ radioactivity. Centrifugation was carried out with a Sorvall RC2B type centrifuge with SS-1 rotor, at 17000 r.p.m. for 5 minutes.

RESULTS

Six groups of experimental data were obtained:

(i) Tyndall value $T.V.$ measured as a function of NaL concentration shows for systems aged for 10 and 100 minutes (AgI 0.001 mol/l = $n^i$, 0.001 M NaI = $n^L$, $\alpha = n^i/n^L = 1$) two pronounced maxima: one at 0.0005 M NaL and another at 0.008 M NaL ,and one small maximum at 0.00004 M NaL (Figure 1). By ageing of the systems the Tyndall maxima broaden so that after $t_A = 10000$ minutes two minima at 0.0001 M NaL and 0.005 M NaL are reached.

(ii) The results of electron microscopy carried out on systems with varying NaL concentration (0.00001 M, 0.0001 M, 0.0005 M, 0.001 M and 0.008 M NaL) are shown in Figure 2 in comparison with $T.V.$ data obtained with systems aged for 100 minutes. Samples taken in the same way gave different pictures of sol density with maximum density at NaL concentration corresponding to the $T.V.$ maximum at 0.0005 M NaL. Sol density is lowest at the second $T.V.$ maximum (0.008 M NaL). As very small particles, silver iodide tetrahedra, octahedra and hexagonal plates can be differentiated in micrographs of sols with both 0.00001 M and 0.0001 M NaL in the systems.

(iii) The results of particle size determination on sols aged for 100 minutes (Figure 3) indicate a decrease of particle size with increasing NaL concentration. The nonlinearity found shows an inversion in the positions of maxima and minima of $\beta R(\text{Å})$ vs. log $c$ (M) NaL curve in comparison with the $\beta T.V.$ vs. log $c$ (M) NaL curve. The size of flocs and suspension density are not coherent with respect to crystallite sizes as shown in Figure 3. The particle size as a
function of NaL concentration has minima in the same regions where the T. V. maxima occurred and vice versa. X-Ray analysis indicate that the mean crystallite size is $R = 548$ Å for systems with 0.0000001 M, 0.000001 M, 0.0001 M NaL; $R = 410$ Å at 0.00001 M NaL; $R = 275$ Å at 0.0005 M NaL and $R = 322$ Å for systems with 0.001 M to 0.008 M NaL. The fraction of hexagonal Agl decreases from $\%H = 53$ at 0.0000001 M NaL to $\%H = 39$ at 0.008 M NaL in the system.

(iii) All negative electrophoretic mobility data plotted against NaL concentrations in Figure 3 follow a similar course as the T.V. data.

(v) Resistivity data (Figure 4) indicate a critical micellar concentration value of $c_M = 0.004$ M NaL solution aged for 100 minutes.

(vi) Surface tension measurements carried out on NaL solutions (Figure 5) yield for the critical micellar concentration values from $c_M = 0.0033$ M to 0.0038 M NaL at given conditions; for the NaL solution with acidity adjusted to pH = 10 and containing 0.001 M NaI the value $c_M = 0.002$ M NaL was obtained.

(vii) Radiometry data show approximately complete sedimentation ($f_s = 0.92 \pm 0.09$) of AgI indicating very low solubilization.

**DISCUSSION**

Monovalent inorganic ions at the concentration of 0.1 M at room temperature cause complete coagulation of negative stable silver iodide sols in aqueous media containing an excess of iodide ions from pH = 1 to ca pH = 10 within a wide range of acidity of the colloid system. Surfactant ions cause an equivalent decrease of colloid stability, i.e. flocculation at concentrations about one thousandth of the concentration of inorganic ions. As a colloid interaction, the effect of inorganic ions on colloid particles is mainly due to the electrostatic compensation of particle charge giving an adequate new quality to the colloid system predominantly characterized by the drop of colloid stability. In systems involving surfactants, the electrostatic interaction in the flocculation process results in a drop of colloid stability too, but it is only the first step of interactions between the surfactant ion and a colloid particle. The analysis of the dependence of turbidity on the concentration present inorganic or surfactant ions give the typical Tyndall maxima, with corresponding critical concentration limits within which lie various critical concentrations determining surface tension change, adsorption-desorption equilibria, critical exchange rates and reversal of zeta potential. The colloid stability of silver halide colloids is also dependent on nonionic surfactants, and the stability of a negative silver iodide sol depends on the concentration of anionic surfactant. The data obtained by various techniques indicate that sodium n-laurylsulphate causes a change of the colloido-chemical properties of negative silver iodide sols by influencing the equilibria between embryos and nuclei and between the nuclei and primary AgI particles. These phenomena are dependent on the surfactant concentration according to the results shown in Figure 1. Such type of interaction between negative colloid particles and the anionic surfactant ion can be explained by van der Waals attractive forces between the colloid particle and the hydrocarbon tail, although this cannot explain the appearance of T.V. maxima. The changes of the Tyndall values with ageing of the systems is not in agreement with the conventional opinion that surfactants hinder the crystal growth. The results described here can be explained by taking into account
the formation of associates in the surfactant solution\(^7\). At very low surfactant concentrations, the direct interactions between primary colloid structures and surfactant ions or associates is of a very dynamic character, and very probably quite different from the interactions in the case of an aged system. In such a case van der Waals interactions are responsible for the processes of transformation of the first colloid structures into stable colloid particles by ageing as has been shown for systems with up to ca 0.00001 M NaL. By adding the cationic precipitation component (silver nitrate solution) to the anionic (sodium iodide solution) containing surfactant at concentrations over ca 0.00003 M NaL the primary silver iodide structures are formed in the medium containing surfactant associates. The very dynamic nature of surfactant associates help us in explaining the resulting interactions\(^8\). If silver iodide ionic pairs are not formed in a palisade adsorption region\(^9\), surfactant associates in contact with primary colloid structures, because of their dynamic quality, lose certain amounts of NaL by bonding at the colloid particle surface. Such type of associate »decomposition« is measured in the »AgI + rhodamine 6 G« systems\(^10\) as formation of a mixed colloid system. In a certain way by preparing systems »in statu nascendi« the surfactant associates promote the transformation of primary structures by direct interactions, and silver iodide particles cause the aggregation of the surfactant associates\(^8,10\). Mutual aggregation results in the formation of a Tyndall maximum; the observed samples have maximum stability (lowest change by ageing) at concentrations higher than 0.0005 M and 0.008 M NaL. Although the Tyndall maxima are obtained for both 0.0005 M and 0.008 M NaL concentrations, the real density of colloid particles are markedly different as shown in electronmicrographs (Figure 2). In both cases crystallite sizes of silver iodide are smaller than in systems with NaL present at lower concentrations (Figure 3) as in the silver iodide suspensions containing sodium laurylsulphate\(^4\). A different electronmicroscopic picture of the analysed systems is probably a consequence of the fact that for the results obtained at 0.008 M NaL the transformation of NaL ions and associates or aggregates into micelles must be taken into account since the critical concentration for micelle formation lies between \(c_M = 0.002\) M NaL (ring method, Figure 5) and \(c_M = 0.004\) M NaL (resistivity data for pure NaL solution, Figure 4). Thus the maximum at 0.0005 M NaL corresponds to the formation of a colloid system with NaL structures below \(c_M\) and the second maximum at 0.008 M NaL corresponds to the formation of a mixed colloid system because silver iodide particles and NaL micelles or aggregated micelles are present in the systems (silver iodide is not markedly solubilized since the sedimentation factor \(f_s = 0.92 \pm 0.09\) is obtained). Smaller crystallite sizes of AgI at NaL concentrations above 0.001 M are probably a consequence of a decreased diffusion or another transport process in a medium involving surfactant aggregates and micelles. Silver iodide particles, partially surrounded by surfactant ions adsorbed at the crystallite/solution interface or with adsorbed higher amounts of NaL have negative electrophoretic mobility in all observed systems. Coincidence of the »T.V. vs. log c (M) NaL« curve with the »w vs. log c (M) NaL« curve (triangles and full circles in Figure 3) confirms the above consideration. For instance at the T.V. maximum at 0.0005 M NaL the smallest crystallites (\(R = 275\) Å) are formed and they are surrounded by the largest amount of NaL ions or molecules so that for the smallest particles electrophoretic mobilities lower than for the systems with 0.0001 M
or 0.001 M NaL are obtained thus indicating interesting mutual colloid interactions in the colloid systems containing surfactant ions or higher structures as similiions (ions of the same sign of charge as the colloid particles)\textsuperscript{11}.

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REFERENCES


SAZETAK

O negativnom solu srebnog jodida u otopinama natrijevog n-laurinata

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Ovaj rad opisuje fizičko kemijsku studiju međudjelovanja između anionskog tenniza natrijeg n-laurinata, NaL, i negativnog stabilnog srebnog jodida pripremljenog »in statu nascendi« s naglaskom na kolidna svojstva sistema u vodenoj sredini. 0.001 mol/l negativnog stabilnog srebnog jodida sadržavalo je u otopini od 0.0000001 M do 0.01 M NaL na 20 °C. Mjerenje zamucenja pokazuje dva izrazita tyndallometrijska maksimuma; elektronska mikroskopija i rendgenska difrakcija analiza pokazuju ovisnost veličine kristalita i gustoće sola o koncentraciji NaL. Dobiveni rezultati pokazuju na sistemima istraživanim u toku starenja, da se za negativne čestice stabilnog sola srebnog jodida pripremanog »in statu nascendi« mogu pretpostaviti različita međudjelovanja sa NaL u otopinama ispod i iznad kritične micelarnih koncentracije.