

Electrical Double Layer on Silver Iodide and Overcharging in the Presence of Hydrolyzable Cations*

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Previous studies on the surface charge and electrokinetic charge on silver iodide as a function of the pAg in the presence of some monovalent and trivalent cations as the counterions were extended to include the influence of pH. The main reason for this study was to investigate the possible propensity of overcharging by adsorption of hydrolyzed counterions. It was found that for K⁺ as the counterion the double layer properties could be well represented in terms of a simple Gouy-Stern model, without accounting for hydrolysis. However, with Al³⁺ or La³⁺ as the counterions, adsorption of hydrolyzed species takes place when the pH is high enough, leading to electrokinetic charge reversal.

INTRODUCTION

The main motivation for starting the present investigation is in the interpretation of overcharging, *i.e.* the phenomenon that in an electric double layer more countercharge is found close to the surface than there are charges on the surface. Briefly, for the interpretation of the phenomenon disparate explanations have been offered and it appears appropriate to study systems, which might allow discrimination. The silver iodide system offers itself as a promising object.

To experimentally detect and quantify overcharging, two types of surface charge density must be simultaneously available, *viz.* the real surface charge, σ^o , and the electrokinetic charge, σ^{ek} . In fact, electrokinetics are the usual procedures to detect overcharging because by these

techniques the charge and charge sign of the outer, mostly diffuse, part of the double layer are measured. Admittedly, there is some uncertainty about the position of the slip plane (if it is not a thin slip layer), but this is mostly a minor issue as compared to the detection of the sign of the outer part of the countercharge and quantifying it. Overcharging can in principle also be inferred from interaction studies, but here determining the sign of the charge is only indirect. Sometimes for overcharging the less precise term »charge reversal« is used. This term stems from electrokinetics. Typically, when to a charged system an agent is added that produces overcharging, the sign of σ^{ek} reverses, hence the name. However, this name is not sufficiently rigorous because it suggests a change of the sign σ^o , which does not take place at all. In fact, upon overcharging the absolute value of σ^o mostly

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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increases without changing sign. Therefore, we avoid the term »charge reversal« except when it is evident that we are dealing with reversal of the electrokinetic charge.

The phenomenon of overcharging is known for over a century. As long ago as 1906 Freundlich mentioned it in one of the first versions of his *Kapillarchemie*, but later he suppressed mentioning it because he learned that it is not the general mechanism by which particles become charged. In 1941 Troelstra defended his PhD thesis »Uitvlokkung en Omlading« (Flocculation and Charge Reversal) at the Utrecht University, Netherlands. His work involved the AgI system and contained a first hint of the possibility of overcharging by the adsorption of hydrolyzed species. However, it was rather qualitative. Below we shall return to this work. Nowadays, abundant numbers of papers contain experimental illustrations of overcharging. Well-known evidence stems from the domain of the adsorption of ionic surfactants and/or polyelectrolytes. For instance, it is easy to let so much CTAB adsorb on negatively charged polystyrene latex that the adsorbed charge overcompensates the charge on the surface. In this case, hydrophobic bonding is the driving force. Similarly, polyelectrolytes can readily adsorb on a surface when the segment adsorption (Gibbs) energy exceeds a low critical value, say of a few tenths of a kT . In the present paper we address the more subtle, and perhaps more elusive, overcharging by simple ions. The driving force for such a type of overcharging is subject to debate.

According to one group of investigators, the origin has to be sought in so-called *specific adsorption*, which is a general term accounting for non-Coulombic attractions between ion and surface. Specific adsorption includes hydrophobic bonding and other water structure-mediated interactions, hydrogen bonding, complex formation and stronger chemical interactions with the surface. For the sake of argument we shall call such interactions collectively »chemical«, even if these have a partly physical nature.

The alternative group seeks an interpretation in terms of *ion correlations*. The main line of thinking is that, because of the discrete nature and finite sizes of the ions in the double layer, their distribution near a charged surface leads to spatial and electric correlations, which under certain conditions leads to situations with overcompensation of the surface charge. For the sake of argument, we denote these phenomena as »physical«.

Both groups have a good point, hence the question who is right. In fact, it is imaginable that both are right, but under different conditions regarding the salt concentration and surface charge. Closer inspection of facts and interpretations is needed. The experimental question is to devise a system for which data could be obtained that would contribute to such discrimination. We shall show that the AgI system offers such possibilities.

LITERATURE REVIEW AND MOTIVATION

A scan of the available literature indicates that the two groups mentioned above can, according to their approach, be roughly divided into »chemists« and »physicists«. Both groups have to deal with the experimental observation that for the interpretation of several double layer properties the Gouy-Chapman theory appears inadequate. This theory is based on the Poisson-Boltzmann (PB) equation. The most obvious defects of PB theory are the assumption of a mean field, the neglect of ion size and of specific bonding. However, the two groups differ radically in their way to deal with these imperfections.

The former group mostly starts with experimental evidence on electric double layers. Their approach is rather pragmatic in that they assume that the deviations from PB behaviour are significant only in the first few water layers close to the surface. The elaboration mostly comes down to add a Stern layer, or some variant of it, involving specific adsorption. Specific adsorption Gibbs energies, also denoted as specific adsorption potentials, are essentially fitting parameters. Their values are rather low, say a few kT units at most. Only for real chemical bond formation these energies are higher. When experiments can be explained in the framework of such a model with a specific adsorption energy that is independent of the surface charge and the salt concentration, there is little reason for considering alternatives.

On the other hand, »physicists« prefer to start from the fundamental side, setting up sophisticated models in which the discrete nature of the ions in the double layer is made explicit. This approach is rather academic, but several groups of investigators have convincingly shown that under suitable conditions ion correlations can give rise to overcharging.

The »physical« interpretation did not really reach the attention of the »chemists«. There are two reasons for that. The first is that overcharging by ion correlations is predicted to occur only for high surface charges in the presence of counterions of higher valency and higher salt concentrations. Under those conditions hydrophobic colloids are typically unstable, so that electrophoresis is no longer a suitable technique. The second reason is that the »physicists« tend to publish in physical journals only, in this way increasing the threshold. Perhaps it must be added that the »physicists« have little knowledge of the relevant physicochemical literature; at any rate the present authors have not yet seen attempts to interpret double layer data in terms of ion correlation theories and critically comparing the results against those obtained by the specific adsorption model.

This takes us to the experimental evidence. There is not so much of it available that can be used as a basis for discrimination. As stated, systems are needed in which σ^o and σ^{ek} can be simultaneously measured. Perhaps the best-studied electric double layer is that at the mercury-

solution interface.¹ However, electrokinetic measurements with mercury are forbiddingly difficult. One of the best-studied colloidal systems is that of the oxides, on which σ^0 values can be obtained that are high enough to expect ion correlations to play a role. A typical systematic study stems from James, Wiese and Healy.^{2,3} For rutile and silica these authors convincingly showed by electrokinetics and stability studies that overcharging by some bivalent and trivalent ions (Co^{2+} , Al^{3+} , *etc.*) occurred because of specific adsorption of hydrolyzed metal oxides. This hydrolysis is pH-dependent. Regrettably, independent σ^0 measurements were lacking, or, for that matter, the acid-base titration needed for determining the charge on the surface measures simultaneously the H^+ uptake or release by the hydrolyzing counterion, so that it is difficult to discriminate. It would be nice if we had a system at our disposal in which the hydrolysis of counterions, and their binding, and the surface charge can be measured independently. The silver iodide system offers such a prospect.

THE ELECTRIC DOUBLE LAYER ON SILVER IODIDE

The advantage of the AgI system is that Ag^+ and I^- ions are charge-determining, whereas the proton is indifferent. So, one can control the surface charge by changing pAg or pI (these two quantities are coupled through the solubility product of AgI) whereas, independently, the extent of hydrolysis of cations can be controlled by changing pH.

For this system much information is available. One of the present authors^{4,5} has obtained σ^0 (pAg) curves, published as differential capacitances

$$C = (\partial\sigma^0 / \partial\psi^0)_{c(\text{salt}),T} \quad (1)$$

Here, the change in the surface potential, $\partial\psi^0$ is obtained from the change in pAg following

$$d\psi^0 = (RT \ln 10 / F) dp\text{Ag} \quad (2)$$

This last equation is essentially Nernst's law, of which the applicability to the AgI system was proven. A vast amount of information has in the mean time been assembled for this system.^{5,6} From time to time related publications appear.⁷ For the present problem two things can be mentioned:

(i) A thermodynamic analysis has been developed to analyze the Esin-Markov coefficient β , defined through

$$\beta = (\partial p\text{Ag} / \partial \log a_s)_{\sigma^0} \quad (3)$$

where a_s is the mean activity of the indifferent electrolyte. The Esin-Markov coefficient is an experimentally accessible parameter. It is a measure of the screening of

the surface charge by the countercharge. In comparative analyses of different screening mechanisms, in particular those leading to overcharging, this coefficient appears a promising double layer characteristic. For the AgI system theory and elaborations are available.⁸

(ii) The literature on overcharging goes back to the work by Troelstra, mentioned before.⁹⁻¹¹ Although this work was only embryonic, it contains an element that has spurred later developments, namely the concept that electrokinetic charge reversal could be realized by specific adsorption of hydrolyzing cations. At Troelstra's time it was not yet entirely clear where the surface charge came from, let alone that it could be measured. This gap was partly filled by the investigation of Ref. 4, but as the proton was known to be indifferent, no reason was felt for controlling the pH.

The logical next step offering itself is to extend these measurements and pay particular attention to the effect of pH on the double layer properties when the solution contains hydrolyzable cations.

By measuring the surface charge and zeta-potential of silver iodide as a function of concentration of charge-determining ions at constant indifferent electrolyte concentration and constant solution pH we present in this paper consistent data set on the effect of hydrolyzed species on the surface charge density of AgI, *p.z.c.* and *i.e.p.*

MATERIALS AND METHODS

Materials

The silver iodide precipitate was prepared by slow addition of 0.1 mol dm^{-3} AgNO_3 solution to a well-stirred 0.1 mol dm^{-3} KI solution.⁶ The addition of AgNO_3 was stopped when the point of zero charge was reached and the sol coagulated completely. After several washes with de-ionized water, the precipitate was aged three days at 80°C and then two months in a solution of $\text{pI} = 4$. The aging causes the specific area of precipitates to decrease; it was continued till the area became constant. The surface area of silver iodide precipitates measured by electrochemical methods (negative adsorption, capacitance) and dye adsorption is in the range $1.0\text{--}1.6 \text{ m}^2 \text{ g}^{-1}$. In our calculations we assumed the surface area to be $1.4 \text{ m}^2 \text{ g}^{-1}$ and this gave good consistency with our previous results.⁶

Water was purified using a Barnstead ultra pure water system.

The salts KNO_3 , AgNO_3 , KI, $\text{Ca}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and $\text{La}(\text{NO}_3)_3$ were received from Merck and were of pro analysis quality. $\text{Zn}(\text{NO}_3)_2$ was received from Aldrich.

Methods

Electrophoretic mobilities were measured with a Malvern Zetasizer device. The method and the data analysis used by Malvern Instruments are described elsewhere.^{12,13} To

suppress electrode polarization a relatively low frequency alternating electric field was applied and the readings were taken at the stationary level.

The mobilities of silver iodide particles were measured in $1 \text{ mmol dm}^{-3} \text{ KNO}_3$ solution as a function of pH and pAg. The average radius of the particles obtained from dynamic light scattering experiment was 300 nm. To calculate the zeta-potential Henry's equation was applied ($\kappa a = 1.5$).¹⁴ In the conversion the excess surface conduction was neglected.

The surface charge was measured with a Wallingford automated titration device. The surface charge of the silver iodide suspension is controlled by the equilibrium Ag^+ or I^- concentrations in solution. To measure this, a silver-silver iodide electrode was used together with a silver-silver chloride electrode as the reference. To ensure reproducibility three silver-silver iodide electrodes were put into the titration cell and their potentials compared.

The whole titration data set was performed with one batch of AgI suspension. To conduct the experiments a certain amount of $1 \text{ mol dm}^{-3} \text{ KNO}_3$ and $0.01 \text{ mol dm}^{-3} \text{ HNO}_3$ or $0.01 \text{ mol dm}^{-3} \text{ KOH}$ were added to silver iodide suspension (2–2.5 g per 50 mL solution) to obtain $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$ concentration and desired pH value. Then the suspension was first titrated with $0.01 \text{ mol dm}^{-3} \text{ AgNO}_3$ up to $\text{pAg} = 4.5$. This was the starting point for all titration experiments. Two titration cycles have been performed in $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$ with $0.01 \text{ mol dm}^{-3} \text{ KI}$ to $\text{pAg} = 11.5$ and back with AgNO_3 to $\text{pAg} = 4.5$ before a given amount of trivalent ions was added. Before and after sample titration, calibration experiments were performed.

Some experiments were conducted twice and were found to be reproducible within 3–5 %. The hysteresis between AgNO_3 and KI titrations was negligible and this was another test of reproducibility.

To obtain the point of zero charge of silver iodide, first the surface charge of silver iodide was detected at three KNO_3 concentrations in the absence of bi- or trivalent cations and the common intersection point established. Having obtained this pristine p.z.c., the relative surface charge curves were transformed into absolute surface charge curves.

EXPERIMENTAL RESULTS AND DISCUSSION

Surface Charge

In Figure 1 σ^0 vs. pAg curves in KNO_3 are compared with those obtained before.⁶

There are some differences between the position of the p.z.c. and surface charge values. In our experiment the p.z.c. equals 5.8 (instead of 5.6 which is mostly presented in literature and which we found in our early

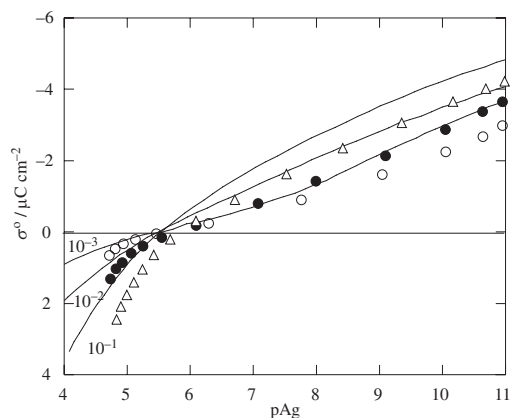


Figure 1. Surface charge of silver iodide as a function of the Ag concentration at different concentrations of KNO_3 measured at $\text{pH} = 5.8$. For comparison data taken from Ref. 6 are also shown (solid lines).

work) resulting in a difference of the surface charge below 20 %.

The surface charge does not depend on solution pH. At low salt concentration the surface charges measured

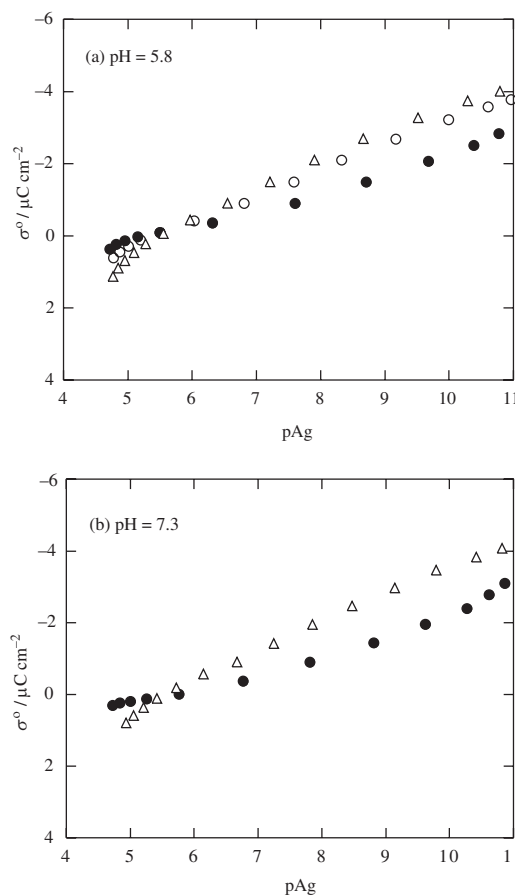


Figure 2. Surface charge of silver iodide in $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$ measured at $\text{pH} = 5.8$ (panel (a)) and $\text{pH} = 7.3$ (panel (b)) as a function of the Ag concentration in the absence (closed symbols) and in the presence of $\text{La}(\text{NO}_3)_3$ (open symbols). $\text{La}(\text{NO}_3)_3$ concentration: $\bullet - 0 \text{ mol dm}^{-3}$, $\circ - 10^{-4} \text{ mol dm}^{-3}$, $\triangle - 10^{-3} \text{ mol dm}^{-3}$.

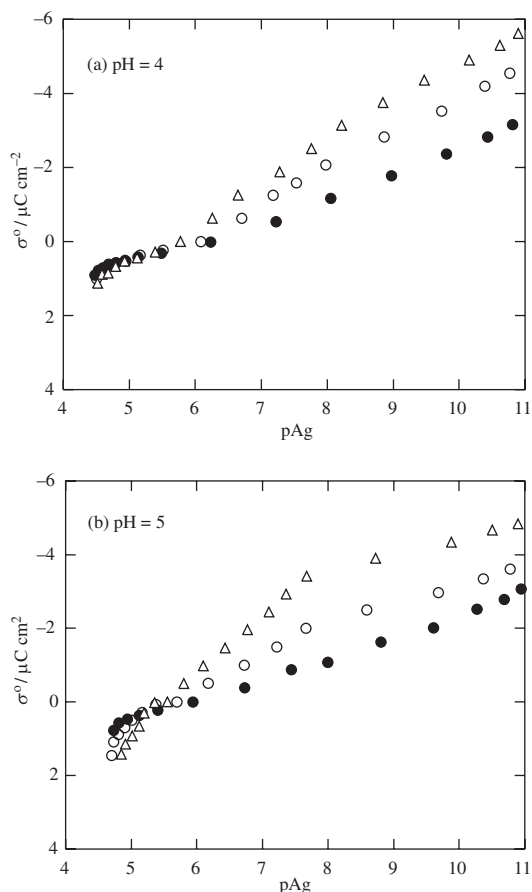


Figure 3. Surface charge of silver iodide in 10^{-3} mol dm^{-3} KNO_3 measured at pH = 4 (panel (a)) and pH = 5 (panel (b)) as a function of the Ag concentration in the absence (closed symbols) and in the presence of $\text{Al}(\text{NO}_3)_3$ (open symbols). $\text{Al}(\text{NO}_3)_3$ concentration: ● – 0 mol dm^{-3} , ○ – 10^{-4} mol dm^{-3} , Δ – 10^{-3} mol dm^{-3} .

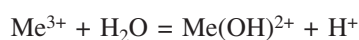
at pH = 4 and 5.8 were nearly indistinguishable at given pAg (not shown).

The surface charge of silver iodide in 10^{-3} mol dm^{-3} KNO_3 in the absence and in the presence of trivalent electrolytes as a function of pAg was measured at pH = 5.8 and 7.3 for lanthanum nitrate and at pH = 5 and 4 for aluminum nitrate. The results are presented in Figures. 2 and 3, respectively.

These rather high concentrations of trivalent salt were chosen to ensure obtaining the effect of hydrolyzed cations on surface charge adaptation and the shift of the p.z.c.

The hydrolytic reactions of Al^{3+} and La^{3+} have been extensively studied because of their use in water treatment. It was shown that their speciations are affected by pH, salt concentration, type of anion, aging, etc.

The first hydrolysis constant of hydrolytic reaction



is defined as

$$K_{1,\text{H}} = [\text{Me}(\text{OH})^{2+}] [\text{H}^+] / [\text{Me}^{3+}] \quad (4)$$

For Al^{3+} $\text{p}K_{1,\text{H}} = 5.0$, Ref. 15; for La^{3+} $\text{p}K_{1,\text{H}} = 8.6$, Refs. 16 and 17. These values indicate that at pH = 8.3 for lanthanum nitrate and at pH = 5.0 for aluminum nitrate more than 50 % of the cations are present in hydrolyzed form. Moreover, the onset of aluminum and lanthanum precipitation starts around these values.

As it is seen from Figures 2 and 3 trivalent cations lead to an increase of the surface charge of both a negative and a positive but they do not considerably affect the position of the p.z.c. The p.z.c. reaches 5.5 when the solution pH approaches the pK values.

In the presence of La^{3+} the surface charge does not increase substantially upon an increase of pH towards the pK value and upon an increase of the lanthanum concentration from 10^{-4} to 10^{-3} mol dm^{-3} . This probably indicates that the saturation level of the surface has been nearly reached.

Quite the opposite, in the presence of Al^{3+} there is a clear tendency of the surface charge to increase upon the rise of both the pH and aluminum nitrate concentration. Another striking feature of Al^{3+} on the surface charge isotherms is that, as it is shown in Figure 3b, the change in slope of the surface charge curves measured at pH = 5 occurs at pAg = 8 for both Al^{3+} concentrations studied and this probably reflects the process of aluminum hydroxide co-precipitation on silver iodide surface.

In fact, a rigorous comparison of the surface charge between Al^{3+} and La^{3+} as the counterions has to be carried out not only at identical pAg values but also at the same composition of hydrolyzed species in solution. The value $\Delta\text{pH} = \text{p}K_{1,\text{H}} - \text{pH}$ can be the reference point for this comparison. This means that roughly the surface charge of AgI measured in the presence of La^{3+} at pH = 7.3 (Figure 2b) can be compared with that measured in the presence of Al^{3+} at pH = 4 (Figure 3a). As one can see, the aluminum effect on the surface charge seems to be more pronounced than that of La^{3+} . This observation, together with the fact that the surface charge in the presence of Al^{3+} continues to rise upon an increase of Al^{3+} concentration in solution at both pH's studied, shows that hydrolyzed aluminum species have a higher adsorption affinity to the silver iodide surface. In the language of Ref. 3 this can also be condensed to the statement that in this range Al^{3+} as the counterion leads to a higher Esin-Markov coefficient than for La^{3+} .

Zeta-potential

The effect of bi- and trivalent cation adsorption on the zeta potential was observed at different pH at pAg = 12.2 in 1 mmol dm^{-3} KNO_3 solution. The zeta-potential of silver iodide measured in 1 mmol dm^{-3} KNO_3 in the absence of hydrolyzed multivalent species in the pH range from 4 to 7 and pAg range from 9.6 to 12.2 did not show any pH and pAg dependence and was in the range between -50 and -60 mV.

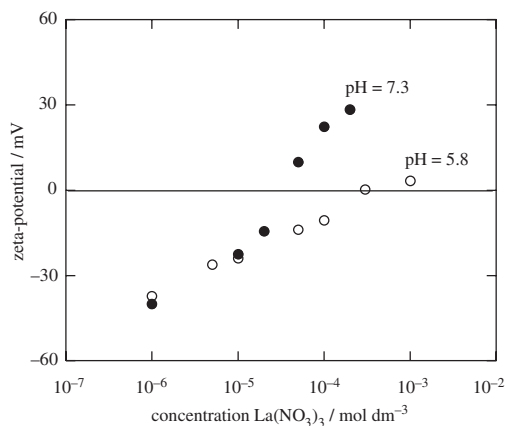


Figure 4. Zeta-potentials measured at pH = 5.8 and 7.3 as a function of the $\text{La}(\text{NO}_3)_3$ concentration. $\text{pAg} = 12.2$; $c_{\text{KNO}_3} = 1 \text{ mmol dm}^{-3}$.

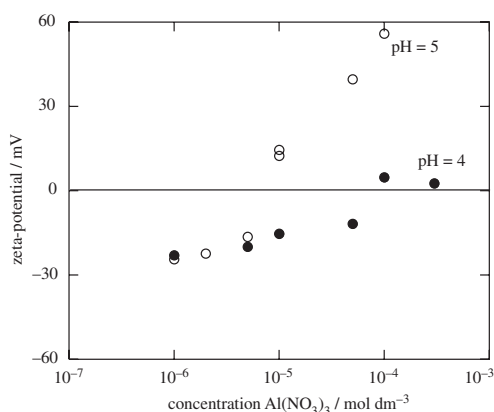


Figure 5. Zeta-potentials measured at pH = 4 and pH = 5 as a function of the $\text{Al}(\text{NO}_3)_3$ concentration. $\text{pAg} = 12.2$; $c_{\text{KNO}_3} = 1 \text{ mmol dm}^{-3}$.

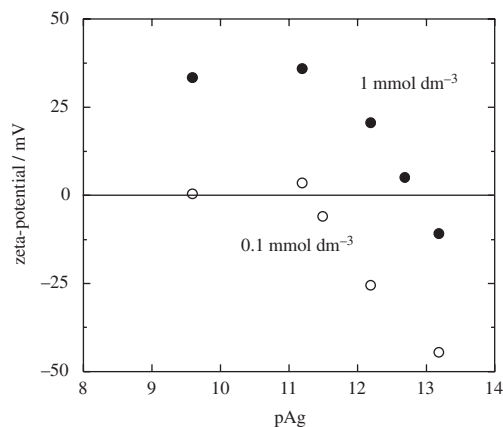


Figure 6. Zeta-potentials measured in 0.1 mmol dm^{-3} and 1 mmol dm^{-3} $\text{La}(\text{NO}_3)_3$ solutions at pH = 7.

Zeta-potentials measured at $\text{pAg} = 12.2$ as a function of $\text{La}(\text{NO}_3)_3$ and $\text{Al}(\text{NO}_3)_3$ concentrations at different pH values are shown in Figures 4 and 5.

At a given pAg value the zeta-potential for both La^{3+} and Al^{3+} solutions becomes less negative upon an increase of trivalent cation concentration. Above a cer-

tain concentration of La and Al species overcharging occurs. The trivalent cation concentration at which the overcharging takes place decreases upon an increase of pH. The more hydrolyzed the cation species are in solution the lower the amount of them is needed to overcharge the surface.

The effect of the La concentration on the i.e.p. of silver iodide obtained at pH = 7 is shown in Figure 6.

The zeta-potential becomes more positive upon an increase of the $\text{La}(\text{NO}_3)_3$ concentration in solution and the i.e.p. is shifted to higher pAg values. The reason for this direction is that when more hydrolyzed La species are adsorbed on the negatively charged sites of the surface, the pAg has to be increased to reach the situation where there is no charge in the diffuse layer.

As a further proof that the effect of overcharging of silver iodide particles is caused by the presence of hydrolyzed cations, additional measurements in $\text{Ca}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ solutions were carried out. The first hydrolysis constant for these cations are 13.25 and 9.25, respectively.^{18,19}

At the pH values studied, the fraction of hydrolyzed Ca^{2+} species in solutions were extremely small (roughly 0.0001–0.01%) whereas the fraction of $\text{Zn}(\text{OH})^+$ species exceed 50 % at pH = 9. The results are shown in Figure 7.

It is seen that virtually unhydrolyzed Ca^{2+} does not cause overcharging of silver iodide interface at any conditions. The zeta-potential decreases in absolute value upon an increase of the $\text{Ca}(\text{NO}_3)_2$ concentration remaining negative at both pH's studied. On the other hand, the shape of the zeta-potential curves in $\text{Zn}(\text{NO}_3)_2$ solutions depends on pH. Whereas at pH = 7 negative values of the zeta-potential decrease upon an increase of the Zn concentration, at pH = 9 overcharging does take place at $10^{-5} \text{ mol dm}^{-3}$ $\text{Zn}(\text{NO}_3)_2$, when hydrolyzed species are present. This observation is entirely in line with our finding that overcharging is induced by the adsorption of hydrolyzed species.

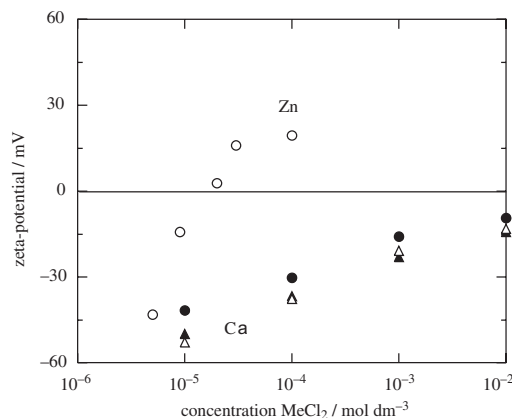


Figure 7. Zeta-potentials measured at pH = 7 (closed symbols) and pH = 9 (open symbols) as a function of the $\text{Ca}(\text{NO}_3)_2$ (o) and $\text{Zn}(\text{NO}_3)_2$ (Δ) concentration. $\text{pAg} = 12.2$; $c_{\text{KNO}_3} = 1 \text{ mmol dm}^{-3}$.

GENERAL DISCUSSION

It is well-known that specific adsorption of ions affects the p.z.c. and the i.e.p. of mineral oxides and ionic crystals. If there is no specific adsorption the p.z.c. and the i.e.p. are identical. Specific adsorption of cations tends to increase pAg (i.e.p.) but to reduce pAg (p.z.c.). The differences between the p.z.c. and the i.e.p. are a measure of the extent of specific adsorption.²⁰

The p.z.c. value we obtained in this work is about 5.6 which is in a range of p.z.c. values presented in literature (5.4–5.7).⁶ Unfortunately, we could not detect the i.e.p. with the laser-Doppler device because direct laser irradiation of an aqueous solutions containing silver salts reduces silver ions through the photolysis of water and the formation of radicals in solution.²¹ With respect to the i.e.p. there is also a general agreement between different authors. The tabulated i.e.p. values collected in Ref. 6 show small deviations in the pAg range 5.2–5.6 probably reflecting minor variations in the surface structure between different samples.

The surface charge curves presented in Figures 2 and 3 show that in the presence of La³⁺ ions the surface charge increases whereas the p.z.c. stays almost the same. Moreover, there is no significant difference between the surface charge measured at different pH and trivalent ion concentrations. However, the more »hydrolyzable« Al³⁺ ion tends to increase the surface charge upon rising the pH and concentration; the change in slope of surface charge curves around pAg = 8 might indicate the onset of precipitation of hydrolyzed species on the surface. Quantitatively, the rise of the absolute value of the surface charge upon specific adsorption is reflected in the Esin-Markov coefficient β (Eq. (3)). This quantity is mainly determined by the amount of charge in the inner (Stern) layer. In the case of specific adsorption of hydrolyzed species β is determined by two opposing trends: hydrolysis reduces β because the charge per ion is lowered but it increases β because of enhanced binding. It appears that in the range of concentrations studied for La³⁺ those two trends more or less compensate each other, whereas for Al³⁺ the increased adsorption of the complex prevails. Further specification of these balances requires more detailed σ^0 (pAg) curves.

On the other hand, the influence of both La and Al adsorption on the zeta-potential and position of the i.e.p. is quite straightforward. See Figures 5 and 6. The reason for the zeta-potential to be so discriminative is that electrokinetically the small difference between the surface

charge and the Stern charge is measured. It is therefore a more sensitive detector of overcharging. At all pH's studied overcharging occurs at a certain concentration of trivalent ions. This concentration tends to decrease upon an increase of pH due to increase of the amount of hydrolyzed species in solution. To check this, an electrokinetic experiment was carried out in the presence of divalent ions Ca and Zn at pH = 7 and 9. As it was mentioned before, the more hydrolyzed Zn ions at pH = 9 show overcharging at 10⁻⁵ mol dm⁻³ concentration whereas the zeta-potential in the presence of the less hydrolyzed Zn ions at pH = 7 and non-hydrolyzed Ca ions demonstrate the 'normal' behavior for mono- and non-hydrolyzed divalent ions. Most likely the hydrolyzed Me(OH)⁺² and Me(OH)⁺ species have a strong affinity to the AgI surface.

If we compare zeta-potentials-(Al(NO₃)₃ and Zn(NO₃)₂ concentration) curves at pH-values close to their pK, we can note that the concentration at which overcharging takes place is nearly the same for both salts and it is close to 10⁻⁵ mol dm⁻³. Perhaps this means that the affinity of Zn(OH)⁺ is higher than that of Al(OH)⁺².

As seen in Figure 6, the adsorption of hydrolyzed cations shifts the i.e.p. towards higher pAg values. If we consider the shift of the i.e.p. as a measure of the specific adsorption, the values (Δ pAg)_{i.e.p.} = 6.0 and 7.5 for 10⁻⁵ and 10⁻⁴ mol dm⁻³ La(NO₃)₃ reflect a high affinity of hydrolyzed multivalent ions to AgI. This correlates well with results obtained for some metal oxides (Fe and Cr) in the presence of multivalent ions. Strong adsorption of hydrolyzed multivalent ions was detected in the range of pH = 6 to 10; it resulted in a shift of the i.e.p. of these oxides towards higher pH.^{22–24}

It is obvious that electrokinetics proves that there is strong adsorption of hydrolyzed La³⁺, Al³⁺ and Zn²⁺ ions on AgI but how does it correlate with the surface charge?

For a number of conditions we have now simultaneously σ^0 (from titration) and $\sigma^d \approx \sigma^c$ available; hence we can obtain the inner charge (or Stern charge) σ^i .

The diffuse charge in mixed electrolyte solutions where each electrolyte *i* dissociate into ν_+ cations and ν_- anions, was calculated using Eq. (5)²⁵, where $y^d = F\psi^d / RT$.

This equation was elaborated for a mixture of a (3–1) electrolyte like Al(NO₃)₃ (component 1, concentration c_1) and a (1–1) electrolyte with the same anion KNO₃ (component 2, concentration c_2). For the diffuse charge equation (6) was obtained.

$$\sigma^d = -(\text{sign } y^d) (2\varepsilon_0\varepsilon FRT)^{1/2} \left[\sum_i c_i (\nu_{i+} e^{-z_{i+}y^d} + \nu_{i-} e^{-z_{i-}y^d}) - \sum_i c_i (\nu_{i+} + \nu_{i-}) \right]^{1/2} \quad (5)$$

$$\sigma^d = -(\text{sign } y^d) (2\varepsilon_0\varepsilon FRT)^{1/2} [c_1 e^{-3y^d} + c_2 e^{-y^d} + (3c_1 + c_2) e^{y^d} - 4c_1 - 2c_2]^{1/2} \quad (6)$$

Table I. The surface and the diffuse charge of silver iodide in mixture of (3–1) La(NO₃)₃ and Al(NO₃)₃ and (1–1) KNO₃ electrolytes. Concentration of KNO₃ is 1 mmol dm⁻³

Component	Concentration mol dm ⁻³	pH	pAg	σ^o $\mu\text{C cm}^{-2}$	σ^d $\mu\text{C cm}^{-2}$	σ^i $\mu\text{C cm}^{-2}$
	0	4.0	9.6	-2.2	+0.4	+1.8
	0	5.8	9.6	-2.1	+0.4	+1.7
	0	7.3	9.6	-2.0	+0.5	+1.5
La(NO ₃) ₃	0.0001	5.8	12.2	-4.5	+0.1	+4.4
	0.001	5.8	12.2	-5.0	-0.1	+5.1
	0.0001	7.3	12.2	(-4.5) ^(a)	-0.2	+4.7
	0.0001	7.3	9.6	(-3.1)	-0.3	+3.4
	0.0001	7.3	11.2	(-4.2)	-0.3	+4.5
	0.0001	7.3	12.2	(-4.5)	-0.2	+4.7
	0.0001	7.3	13.2	(-5.5)	+0.1	+5.4
Al(NO ₃) ₃	0.0001	4.0	12.2	(-6.0)	-0.1	+6.1
	0.0001	5.0	12.2	(-5.0)	-0.5	+5.5

^(a)Values in brackets are obtained by extrapolation of surface charge curves.

In the case that one of the concentrations is zero, this equation reduces to that of the pure remaining compound. Results are presented in Table I.

The data tabulated show that in the absence of trivalent ions 20–25 % of the surface charge is localized in the diffuse part of double layer, the remainder is localized in the inner *Helmholtz* part so that the net charge is zero:

$$\sigma^o + \sigma^i + \sigma^d = 0 \quad (7)$$

In the presence of trivalent ions due to specific adsorption there is more positive charge in the inner layer than required to compensate the surface. Specific adsorption of ions implies adsorption by non-electrostatic forces. For hydrolyzed tri- and divalent ions the chemical contribution to the Gibbs energy of adsorption probably comes from the attraction between the relatively hydrophobic AgI surface and the hydroxyl groups of hydroxocomplexes.

CONCLUSION

The present study proves beyond doubt that overcharging of AgI surfaces by multivalent cations has a »chemical origin«, *viz.* the adsorption of hydrolyzed species. It is unlikely that in addition to this also »physical« overcharging takes place by ion correlations because the surface charge (less than 4 $\mu\text{C cm}^{-2}$) is too low for that.

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SAŽETAK

Električni dvosloj srebrova jodida i prenabijanje u prisutnosti hidrolizirajućih kationa

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Dosadašnja proučavanja površinskog i elektrokinetičkog naboja srebrova jodida, kao funkcije pAg u prisutnosti monovalentnih i trovalentnih kationa, proširena su na proučavanje utjecaja pH. Glavni razlog za ovo proučavanje je ispitivanje mogućeg prenabijanja površine uslijed adsorpcije hidroliziranih protuiona. Kako je nađeno, jednostavni Gouy-Sternov model, koji ne uzima u obzir hidrolizu, dobro opisuje svojstva električnog dvosloja u slučaju K^+ kao protuiona. Međutim, uz Al^{3+} i La^{3+} kao protuione, do adsorpcije hidroliziranih vrsta dolazi pri dovoljno visokom pH, što dovodi do promjene predznaka elektrokinetičkog naboja.