Electrokinetic Studies in Disperse Systems. VII. Ion Exchange and the Electrokinetic Potential of Precipitates of Silver Iodide

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A systematic study of the influence of exchange of ions on the surface of silver iodide precipitates on the elektrokinetic potential (EKP) was undertaken. Examples of the exchange of ions of valencies 1:2, 1:3, 1:4, 2:4 and 3:4 are given. At higher activity of potential determining ions in solution, at $pI = 3$, larger changes in the EKP were measured. At the same pI effects of specific adsorption of Th^{4+} were found. The conclusion is drawn, that the exchange of ions at the surface bears no direct, simple relation to the EKP.

INTRODUCTION

Relations have been established for the adsorption equilibria of simple ions on the surface of silver iodide precipitates.[1] It was found that silver iodide negatively charged by an excess of iodide ions ($pI = 2$ to $pI = 7$) behaves like an ideal ion-exchanger of low exchange capacity. It was also found that the exchange capacity, and the adsorbed amount of counter ions, is independent of pI and constant in the same concentration region. In the meantime refinements of experimental techniques have been made[4] enabling measurements at high ionic concentrations. It was therefore considered worthwhile to reexamine the electrokinetic potential (EKP) of negatively charged silver iodide.[2,3] Also, it was hoped to establish relations of EKP *vs.* concentration for a given ion when a second ion was present in high concentration.

Surface conductance renders the measurements of EKP of porous diafragms in low concentrations of electrolytes inaccurate, but it could be avoided by using solutions with fixed, high concentrations of a 1-1 electrolyte. Changes of the EKP in these experiments are expected to be small but significant. The influence of a given ion is obtained according to the requirements of the Schulze-Hardy law[5] expressed either as the inverse sixth power dependence[5,6] or, as it has been established in a series of experiments on silver halides[7,8] by the log-lin relationship:

$$C_1/C_2 = 10^{(z_2-z_1)\,a} \qquad \cdots \quad \cdots \quad \cdots \quad (1)$$

$$i.e. \quad \log C_1 = \log C_2 + a\,(z_2 - z_1) \qquad \cdots \quad \cdots \quad (2)$$

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Where the c's and z's denote the relevant critical concentrations and charges of ions 1 and 2, respectively. a denotes the linear Schulze-Hardy rule constant.[7-9] It was hoped to present experimental evidence that in exchange of one ion for another one of different charge in the adsorbed state, according to equation (1), no first order influence on the EKP schould be observed.

<div align="center">EXPERIMENTAL</div>

Silver iodide used in this series of experiments was prepared according to Lange[3] and modified as in a previous communication[2] by precipitation in the isoelectric region ($pAg = 6.2 - 4.5$). $AgNO_3$ was added to NaI solution under vigorous stirring until rapid coagulation was observed. The precipitate was washed by decantation with tripple distilled water up to 20 times till the conductivity of the wash was less than the value for water (CO_2 equilibrated) due to the $H^+ - Na^+$ exchange on the surface of the precipitate. Water was removed from the precipitate by decantation and drying at 50^0 C in vacuum. The dry precipitate was ground and sieved through a 240 Mesh silver wire sieve and stored.
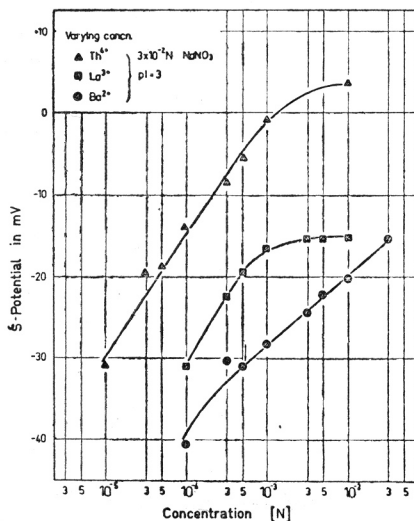

Fig. 1. The EKP — concentration relation for Th^{4+}, La^{3+}, and Ba^{2+} in presence of constant concentration of $NaNO_3$ ($3 \times 10^{-2} N$) and $pI = 3$.

200 ml of solutions were prepared from highest purity grade commercial salts and tripple distilled water. The system was made up to 1×10^{-2} M in dried AgI, and equilibrated with the given electrolyte solution for at least 2 days before taking measurements. The conductivity of the solutions was kept high and constant by addition of a 1 : 1 electrolyte in high concentration. In all the experiments the solutions were made 3×10^{-2} M in $NaNO_3$ or 1×10^{-2} M in HNO_3. La^{3+}, Y^{3+} and Th^{4+} solutions were brought up to $pH = 3$ in all instances in order to prevent influence of hydrolysis. The activity of potential determining ions was chosen in this series of experiments at two values in the negative region, namely at pI 3 and pI 5.

The EKP was measured by the streaming curent technique[4], and calculated from the Helmholtz-Smoluchowski equation:

$$\zeta = (4\eta/D) \ (i/P)x \ R\varkappa\pi$$

Values of $\eta = 0.01$ poise, $D = 80.4$ (dielectric constant of water) were taken as standard values.

RESULTS

From a series of experiments on adsorption and ion exchange,[8,9] the constant $a = 1.7$ was taken. It was the working hypothesis that the predominant counter-ion in the electrochemical double layer will be that one of the two counter-ions whose charge is greater and which is present in a concentration higher than $10^{-\Delta\,za}$ times the concentrations of the other counter-ion. Performing measurements in broad concentration ranges below and above the calculated point of approximate equality of adsorbed amounts of the two ions, the replacement of one ion for the other in the double layer was measured in the changes (if any) of the EKP.
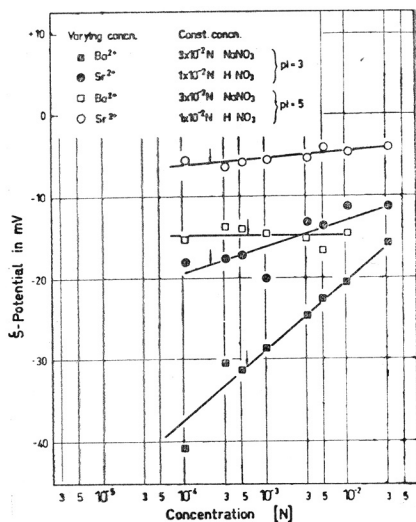

Fig. 2. The EKP — concentration relation showing the exchange of monovalent ions for divalent ones.
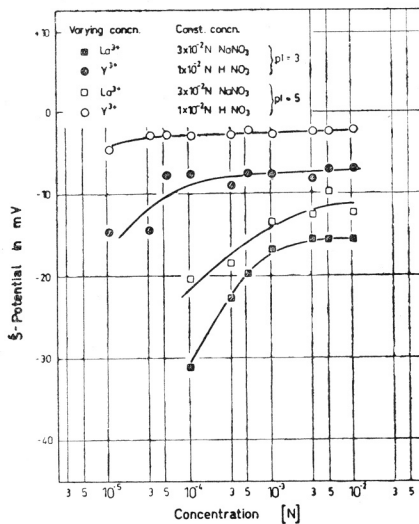
Fig. 3. The EKP — concentration relation showing the exchange of monovalent ions for tri-valent ones.

In Fig. 1 the EKP of AgI, at $pI = 3$, in the presence of 3×10^{-2} M NaNO$_3$ is shown. It was found that the addition of cations of higher charge (Th^{4+}, La^{3+} and Ba^{2+}) lowers the EKP. The influence is exhibited at a lower concentration for the higher charged counter ions. Th^{4+} shows specific influence in reversing the sign of the EKP. This influence is exhibited although the high $pH = 3.0$ precludes formation of hydrolyzates.[10,11] For Ba^{2+} the arrow indicates the equal adsorbed amount of Ba^{2+} and Na^{+}.

In Fig. 2 examples of the 1:2 exchange concentration-EKP relation is shown. Almost no influence of exchange is found at $pI = 5$. At $pI = 3$ the exchange causes a significant linear decrease with the logarithm of the concentration. It is to be noted that H^{+} causes lower potentials than Na^{+}, the cell resistances being in the range of 1 to 2×10^4 Ohms. Thus, the influence of conductivity is excluded.

Examples of the 1:3 exchange are shown in Fig. 3. The influence of tri-valent cations is clearly pronounced. Lower concentrations have not been tried as the concentration range indicated shows remarkable changes in the

EKP. It is seen that the rule is always the same: the higher concentration of potential determining ions shows higher EKP; the change in, and the relative value of, the EKP is smaller for the Y^{3+} — H^+ pair than for the La^{3+} — Na^+.

Figs. 4 and 5 throw more light on the 1 : 4, 2 : 4, and 3 : 4 exchanges. Th^4 reverses the sign of the EKP at $pI = 3$, and not at $pI = 5$, the pH being in both cases approximately 2. For La^{3+} there is no recharge, only the difference between $pI = 3$ and 5 is large.

The 4 : 3 and 2 : 3 relations are shown in Fig. 6. The Ba^{2+} — La^{3+} exchange does not show any influence on the EKP. The comparative experiments with Sr^{2+} — Y^{3+} at $pI = 5$ indicate the required degree of reproducibility and the absence of any specific effects for the bi- and tri-valent cations.
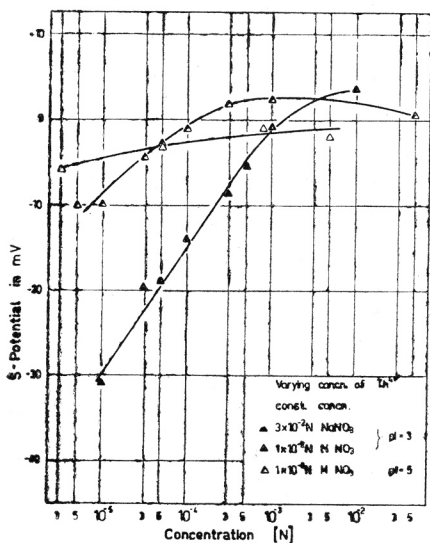

Fig. 4. The EKP — concentration relation showing the exchange of monovalent ions for a quadri-valent ion(Th^{4+}).
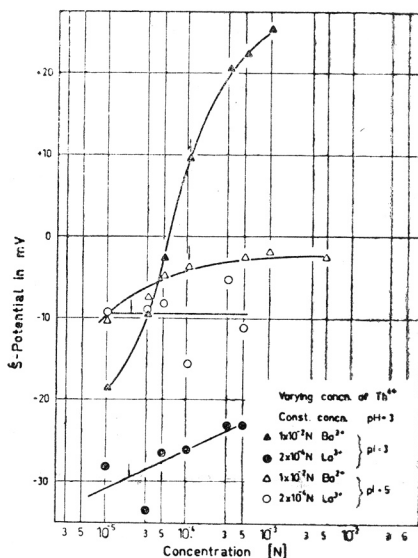
Fig. 5. The EKP — concentration relation showing the exchange of divalent and trivalent ions for the quadrivalent (Th^{4+}) ion. pH = 3.0.

DISCUSSION

The interpretation of EKP has several aspects. If one tries to correlate the experimental ζ and the theoretical ψ_δ potentials various refinements of the simple electrokinetic equation are needed in order to account for the following effects: the dielectric saturation (see however ref. 12) the electro-viscous effect, the position of the plane of shear[13] and the problem of »three capillaries«.[14] Accurate theoretical solutions for these corrections have been obtained only for single capillaries in the streaming techniques, and for the measurements of electrophoretic mobility[15,16]. However, if one makes use of the EKP as a relative indicating parameter the data can then be interpreted in terms of changes in the electrochemical double layer provided sets of

measurements are obtained under analogue conditions. This approach is considered here as the only possible, since we are dealing with diaphragms of precipitates to which none of the suggested corrections can be quantitatively applied. Such an interpretation requires that ionic components of the solutions are strictly defined: the activity of constituent (potential determinig) ions was fixed at one of the two values in the negative activity regions. This provides for the defined, fixed, charge on the surface and for the total adsorption capacity.[1,2] High concentration of an indifferent electrolyte in the solution takes care for the influence of surface conductance, and at the same time provides for the necessary experimental condition of having low internal cell resistance.[4] Finally the pH of the solution was fixed at a point where the hydrolysis of the ion studied is subdued.
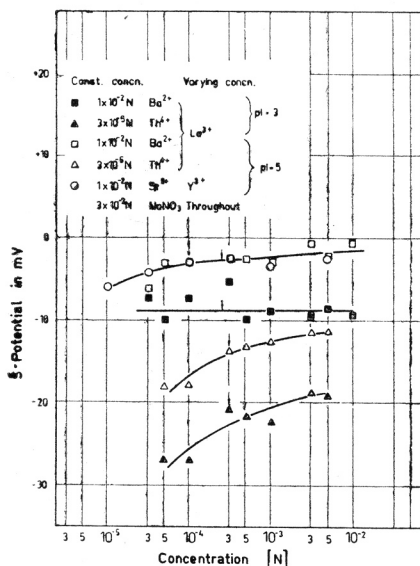

Fig. 6. The EKP — concentration relation showing the exchange of divalent and quadrivalent (Th^{4+}) for the trivalent ones. Concentration of $NaNO_3 = 3 \times 10^{-2}M$; pH = 3.0.

The results indicate the difference in the EKP of the original surface for pI = 3 and 5. This is different from the results of the measurements on precipitates which were obtained by direct precipitation from the solution of the final composition (precipitates *in statu nascendi*). There, only one counter ion should have been considered, and constant EKP and constant adsorption capacity with the change in pI was observed.[1,2] It is clearly seen that in the concentration range studied there was a marked decrease in the EKP for increased concentration only at pI = 3. This effect should be a consequence of increased amount of ion pair forming species (in contrast to »free« counter ions in the outer Helmholtz plane) with increased surface charge. The phenomenon of the reversal of charge by Th^{4+} ion is observed at the lower pI (= 3) value. Even if the pH is low (pH = 3.0) the highly charged Th^{4+} is believed to be partly associated with anions. If the interaction with the surface is brought about by increasing the concentration of Th^{4+} in

the solution attractive forces cause adsorption above coulombic equivalency, thereby producing reversal of sign of the EKP.[10]

It has been long established that H^+ and OH^- do not act as potential determining ions for the AgI system[3,5] In the first instance they act as simple counter ions. Comparative experiments in this paper with Na^+ and H^+ as the primary counter-ions, show that at approximately the same cell conductivity lower potentials are obtained with the H^+ ion. This is in accordance with the higher mobility of the H^+ ion (or of some of its hydrated species at the outer Helmholtz plane). It follows from Fig. 3 and 4 that the flattening of the curve or the reversal of sign is attained at lower concentrations of the exchanging ion with H^+ as partner as compared with Na^+. This quantitative conclusion is valid if we take into consideration the different bulk concentrations of both ions (1×10^{-2} gion/l H^+ vs. 3×10^{-2} gion/l Na^+). With respect to the relative changes in the magnitude of the EKP, least values were obtained with H^+, indicating that the extension of the diffuse layer is considerably smaller in this case. Summarizing the obtained results it may be stated that by the combined influence of two or three counter ions, of which one is present in a variable concentration, no simple relations were obtained. This result is analogous to the result showing the influence of mixtures of counter ions on the coagulation values. Generally, mixtures of ions cause the involved effects and simple additivity was seldom observed.[17]

Examples of absence of any influence of the adsorbed counter-ion valency upon the EKP were found. The general conclusion which can be drawn is, that with the increasing concentration of counter-ions the main influence on EKP occurs in concentration regions which are not directly connected with a single species and its charge.

The error of a single measurement of EKP by the streaming current method used here is estimated to be ±5% or ±0.5mV whichever is the greater. Thus the streaming current technique as applied to porous diaphragms, appears to be a suitable method of measuring EKP at high concentrations of electrolytes.

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IZVOD

Elektrokinetičke studije u disperznim sistemima. VII. Izmjena iona i elektrokinetički potencijal taloga srebrnog jodida

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Mjereći elektrokinetički potencijal taloga srebrnoga jodida metodom struje strujanja promatran je utjecaj zamjene dvaju iona različitog naboja, adsorbiranih na površini. Ustanovljeni su efekti specifične adsorpcije Th^{4+} kao i prenabijanje kod $pJ = 3$. Utvrđeno je da se za istu visoku koncentraciju pratećeg elektrolita elektrokinetički potencijal jače mijenja kod $pJ = 3$ nego kod $pJ = 5$. U slučaju kada je prateći jednovalentni ion u visokoj koncentraciji H^+ dolazi do njegove zamjene kod niže koncentracije viševalentnog iona, ali su elektrokinetički potencijali niži nego što je to slučaj sa Na^+. Sva su mjerenja vršena kod konstantne vodljivosti i pokazano je, da je modificirana metoda mjerenja struja strujanja, za diafragme od ionskih taloga, podesna metoda za studiranje utjecaja ionskog sastava otopine na elektrokinetički potencijal.

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