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Original Scientific Paper

Determination of the Ion Adsorption by the Radioactive Tracer Technique. VI. Counter Ion Adsorption on Silver Iodide in the Equivalency Region*

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Using radioactive $^{152}Eu^{3+}$ and $^{60}Co^{2+}$ indicators the adsorption of these ions on the surface of silver iodide precipitates was measured. The experiments were performed in the equivalency region, from *p*I 5.5 to *p*Ag 5.5. The measurements indicated a constant amount of counter ions of about 2 mgequiv./gmole of AgI adsorbed from *p*I 5.5 to *p*I 7. At higher *p*I a gradual desorption occurs, and at *p*Ag 7.3 the zero point of adsorption is attained. The adsorbed amount is independent of the concentration of the counter ion in the solution in the range from the coagulation concentration up to ten times its value. By aging the precipitate or by some other kind of pretreatment the adsorbed amount of counter ions is decreased. In addition the zero point of adsorption is shifted from *p*Ag 7.3 to *p*Ag 7.1. Series of experments were performed to establish the adsorption-desorption equilibria of one ion in presence of various concentrations of a second one.

INTRODUCTION

Previous papers of this series[1-4] were mainly concerned with the experimental elucidation of the influence of the concentration and valency of counter ions on their adsorbed amounts on silver iodide in the negative stability region. It was shown that the coagulated silver iodide behaves as an ion-exchanger.

The results have shown that the fundamental ion exchange equations apply for the system silver iodide — ionic solution. It was shown also that the same relations are valid whether the total concentration of counter ions is higher, equal, or even lower than the corresponding coagulation value.

All these investigations were restricted to the region of *p*I values od the negative stability region $2 < pI < 6$. It has been also found that the adsorbed amount changes only insignificantly with *p*I. The change in the adsorbed amount can be attributed to the change in the specific surface. At constant dispersity the adsorbed amount of counter ions (that is, the charge per particle ratio) would be constant and independent of *p*I. Therefore one of the main

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problems to be investigated was the problem of the conditions under which, with decreasing pAg values in the isoelectric region, the adsorbed amount becomes equal to zero. In the present paper experiments are described which were performed in order to elucidate the problem formulated above by measuring the adsorbed amount of counter ions in dependence of $pI(-pAg)$ in the equivalency region $(5 < pI - pAg > 5)$. The influence of the counter ion concentration, of the pretreatment of the precipitate, of the time of measurement of the adsorption, of the direction of the activity change ($I^- \rightarrow Ag^+$ or $I^- \leftarrow Ag^+$), and of the concentration of a second counter ion present was established. The results were expressed in gramequivalents of adsorbed counter ion per grammole of AgI, because the results in a.e. coulombs per cm^2 are not reliable. All methods of surface determination are based on the assumption of a constant surface which does not change during the experiment. This assumption cannot be considered valid in general for AgI preparations of any kind.

EXPERIMENTAL

The adsorption of counter ions was measured on fresh *(in statu nascendi)* precipitates and on aged or dried precipitates.

The experiments were performed in two steps. In the first step, a coagulated suspension of AgI was prepared by pouring a solution of $AgNO_3$ into a diluted solution of NaI to which predetermined quantities of one, or two counter ions were added in concentrations higher than the coagulation value. The pI value of this suspension was 5.5. In the second step, by further additions of $AgNO_3$ delivered by an automatic titrator, the pI value was increased in predetermined increments to cover the isoelectric region systematically. Each time, after the pre-selected pI value was reached, a sample of the suspension was taken out. In this way a series of 8 to 9 systems, covering the range from pI 5.5 to pAg 5.5, was obtained. Immediately after the preparation, the solution was labelled with the corresponding counter ion radioactve isotope of a high specific activity. After 12 to 15 hours, the AgI was filtered off, washed, dried, weighed and counted. In this way the adsorbed amounts of counter ions, in gramequivalents per grammole of AgI, were determined as a function of pI. As indicator electrodes calibrated paraffined Ag—AgI electrodes of the electrolytic type[9,10] were used, in connection with a saturated calomel electrode. In the preparation of the systems with fresh precipitates a volume of 500 ml of a $2 \times 10^{-3} N$ NaI solution in a 2000 ml beaker was stirred with predetermined amounts of counter ion nitrates. Along the wall of the beaker, 450 ml of a $2 \times 10^{-3} N$ $AgNO_3$ solution was added from a burette with a constant delivery speed of about 3 minutes per 50 ml. Then the calibrated indicator electrode and the standard electrode were inserted and by further additions of the $AgNO_3$ solution the pI value was adjusted to 5.0. Now the automatic titrator (Radiometer Copenhagen — TTT 1 c) was put into operation as a potentiostat, and from a 2.5 ml syringe further amounts of the $AgNO_3$ solution were added to obtain the pre-selected pI value. Each time the selected pI value was reached a 100 ml sample was transferred to a 250 ml beaker. This procedure was repeated until a series of 8 to 9 systems was obtained covering systematically the isoelectric region.

In parallel to each series of systems a series of solutions of equal pI values was prepared in the same way by titrating a $10^{-5} N$ NaI solution. These solutions were used subsequently for the washing of the precipitates. The drying, weighing and counting of the specimens was performed in exactly the same way as described before[1,2].

Preparation of the »aged« precipitates

The suspension, with a pI value 5 obtained in the described way, was left to age for 24 hours at 20^0, 40^0 and 60^0C. After cooling, the systems with various pI values were prepared as before.

Preparation of the »dried« precipitate

To 1000 ml of a $10^{-5}N$ NaI + $10^{-3}N$ $NaNO_3$ solution, 0.2348 g., corresponding to 1×10^{-3} gramequivalents, of dried AgI was added. The variation of p*I* was carried out as before. The Ag—AgI electrodes[9,10]. The activity of excess I^- and Ag^+ ions was measured by means of rotating paraffined Ag—AgI electrodes of the electrolytic type.

Calibration of the electrodes

The calibration of the electrodes was performed by automatic recording of the plots »electromotive force against added volume« during the titration of the $10^{-5}N$ NaI + $1 \times 10^{-3}N$ $NaNO_3$ solution with a $4 \times 10^{-3}N$ $AgNO_3$ solution. The speed of the titration (time of addition + time of registration) was selected in such a way that the full plot was registered in about 1 hour. No significant influence of lower speeds (up to 8 hours of total titration time) on the plots could be established. Electrodes calibrated in this way were later used for the preparation of the systems with the activity change in the direction $I^- \rightarrow Ag^+$. The electrodes to be used for the inversed $I^- \leftarrow Ag^+$ direction of the change during the preparation of the systems were calibrated in the inverse way.

From the registrated plots 14 to 16 readings »EMF added volume« were taken. The minimum concentration changes which could be read on the chart were 2×10^{-8} gramequivalent per litre. The maximum relative error in the volume readings was 3%. From these excess concentrations of I^- and Ag^+ ions were calculated in such a way that they gave a straight line in the plot »EMF against logarithm excess concentration« with a theoretical slope of 58 mV. In spite of the highest possible care to prepare all electrodes in the same way, only about one half of them gave straight lines as required theoretically.

Solutions and chemicals.

All chemicals used were of annalar or high purity grade. The concentrations of ions in solution were determined by classical analytical methods.

All $AgNO_3$ solutions were prepared by dilution of a $2 \times 10^{-2}N$ stock solution prepared by dissolving a weighed sample of $AgNO_3$ previously dried to constant weight at 105°C. The $2 \times 10^{-2}N$ stock NaI solution was prepared by dissolving NaI and by subsequent determination of its precise concentration by titration with the $AgNO_3$ solution.

The solution of radioactive $Eu(NO_3)_3$ was prepared by dissolving a radioactive sample of Eu_2O_3 (Amersham) in nitric acid (30%). The excess of the acid was evaporated under an infrared lamp and the residue dissolved in $10^{-4}N$ nitric acid.

Analogously a piece of an radioactive Co wire (Amersham) was transformed into the nitrate form.

RESULTS

The results are shown as plots of the adsorbed amount of Eu^{3+} (or Co^{2+}) in milligramequivalents per mole of AgI (ordinate) against *p*I (—*p*Ag) (abscissa). To a good approximation the logarithm of the ionic product of silver iodite is —16, and as a consequence the maximum *p*I and *p*Ag values were taken as equal to 8. Where not otherwise stated, the direction of the activity change was $I^- \rightarrow Ag^+$, that is, the variaiton of the activity was achieved by additions of $AgNO_3$ to suspensions originally contaning an excess of I^- ions.

Figure 1 gives a typical plot of Eu^{3+} adsorbed versus *p*I. The main decrease of the adsorbed amount of Eu^{3+} occurs between *p*I 6 and pAg 7.3. This latter value may be considered as the zero point of charge. This figure shows also that the concentration of added $Eu(NO_3)_3$ from 2.0×10^{-4} up to $1 \times 10^{-3}N$ has no influence either on the shape of the plot or on the zero point of adsorption.

On the basis of these results, the concentration of Eu^{3+} $2 \times 10^{-4}N$ was chosen as suitable for the study of the adsorpion-desorption phenomena. In this concentration AgI coagulated easily and the specific activity was high enough to permit precise measurements.

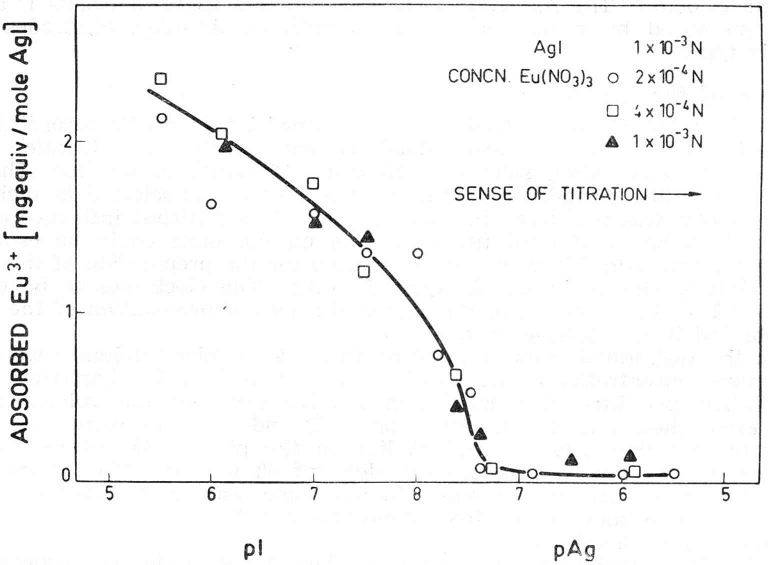

Fig. 1. Quantity of Eu^{3+} adsorbed on silver iodide in dependence of *p*I, and of the concentration of $Eu(NO_3)_3$ in the solution.

Figures 2 and 3 indicate the importance of the pretreatment of the precipitate. The adsorbed amount is highest when the adsorption is measured

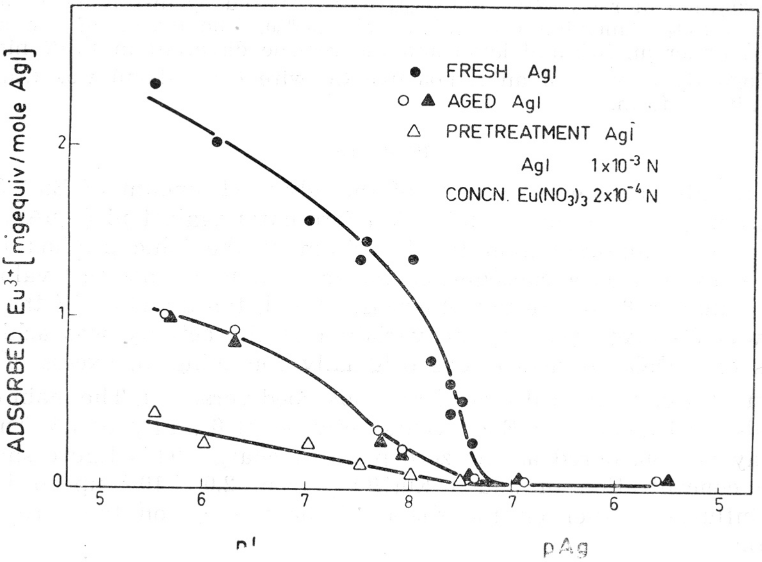

Fig. 2. Influence of pretreatment of silver iodide precipitates (»fresh«, »aged« or »dried«) on the quantity of Eu^{3+} adsorbed. The concentration of $Eu(NO_3)_3$ in the solution was constant, $2 \times 10^{-4} N$.

on »fresh« precipitates. Various methods of aging at different temperatures cause a marked decrease of the adsorption, and, as expected, the adsorption was lowest if »dried« precipitates were used.

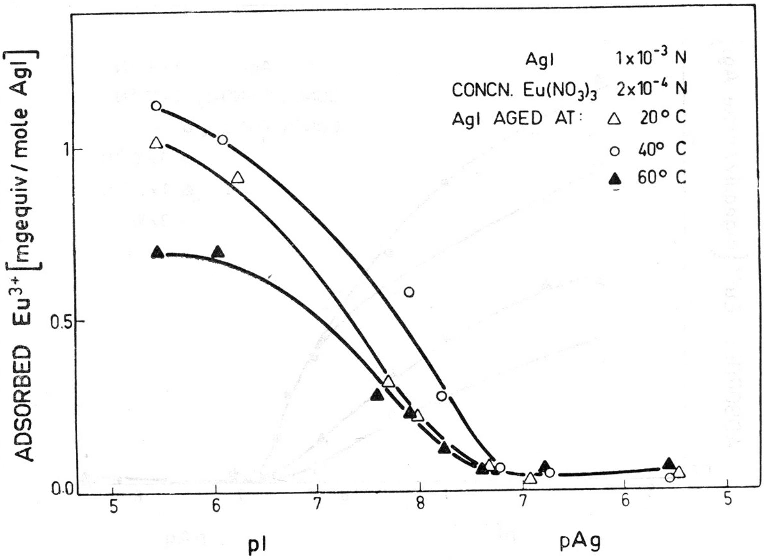

Fig. 3. Quantity of Eu^{3+} adsorbed on silver iodide in dependence of *p*I. Influence of the temperature of aging 20, 40 and 60°C.

Results shown in Fig. 4 indicate the reversibility of the adsorption. With freshly prepared precipitates, and with precipitates aged at *p*Ag 5.5, titrated afterwards with NaI, zero or negligible adsorption up to *p*Ag 7.1 was

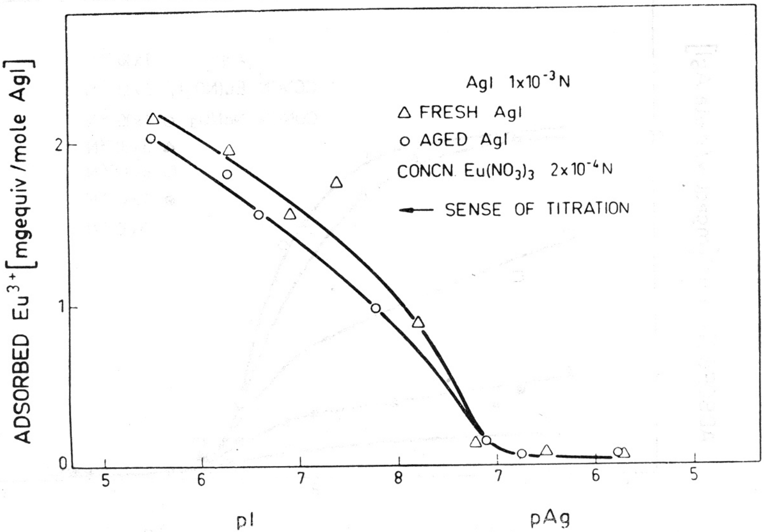

Fig. 4. Quantity of Eu^{3+} adsorbed on »fresh« and »aged« precipitates in dependence of *p*I. Originally positive precipitates titrated with I$^-$.

found. With an increase in the activity of I^- the adsorption of Eu^{3+} increased considerably to a value of *p*I 5.5, and from this value on increased insignificantly (0.25 per *p*I = 1, see refs. 1 and 2).

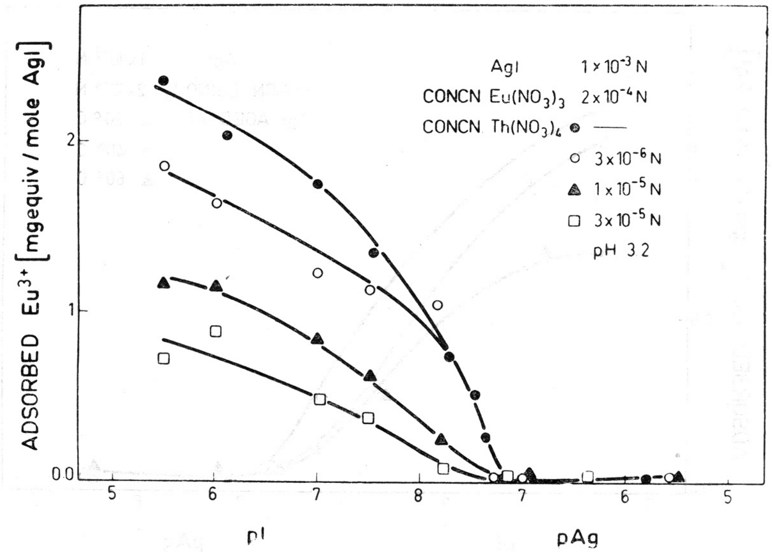

Fig. 5. Desorption of Eu^{3+} by $Th(NO_3)_4$ in dependence of *p*I. Concentration of Th^{4+} varied, pH 3.2.

Figs 5 and 6 show that neither the valency nor the concentration of a second counter ion present (Th^{4+} and Na^+) cause a shift of the zero point of adsorption. The increasing concentrations of these ions (Th^{4+} 3×10^{-6} to

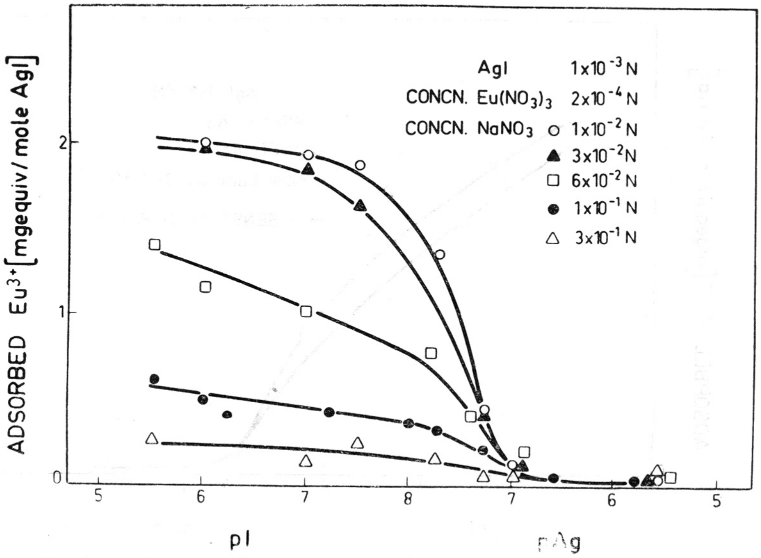

Fig. 6. Desorption of Eu^{3+} by $NaNO_3$ in dependence of *p*I. Concentration of $NaNO_3$ varied.

$3 \times 10^{-5}N$, Na^+ 1.0×10^{-2} to $3 \times 10^{-1}N$) however, cause, a decrease of the adsorbed amount. Equal plots as with Th^{4+} and Na^+ were obtained with La^{3+} and Sr^{2+}.

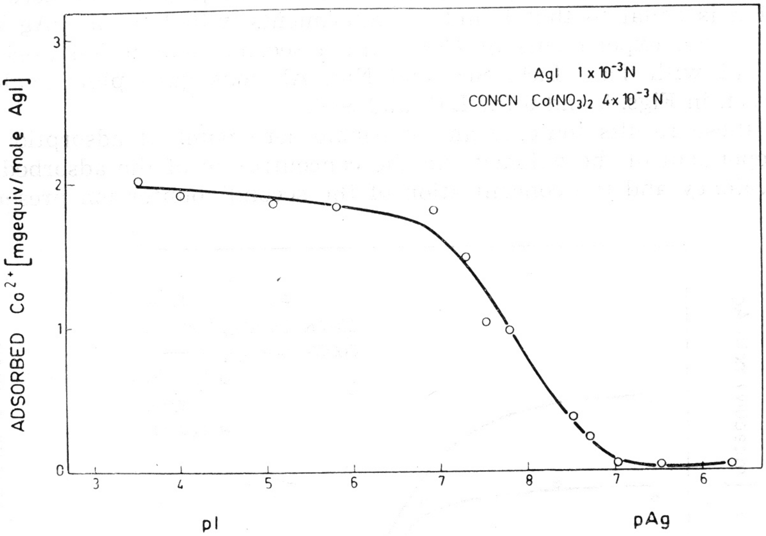

Fig. 7. Quantity of Co^{2+} adsorbed in dependence of pI. Constant concentration of $Co(NO_3)_2$ in solution: 4×10^{-3} N.

In order to obtain some information on whether the observed regularities in the adsorption of trivalent ions are of a general nature, a series of experiments using the radioactive Co^{2+}-60 ion was performed. In Fig. 7 a typical plot for the variation of the adsorbed Co^{2+} in the region pI 3.5 to pAg 5.5

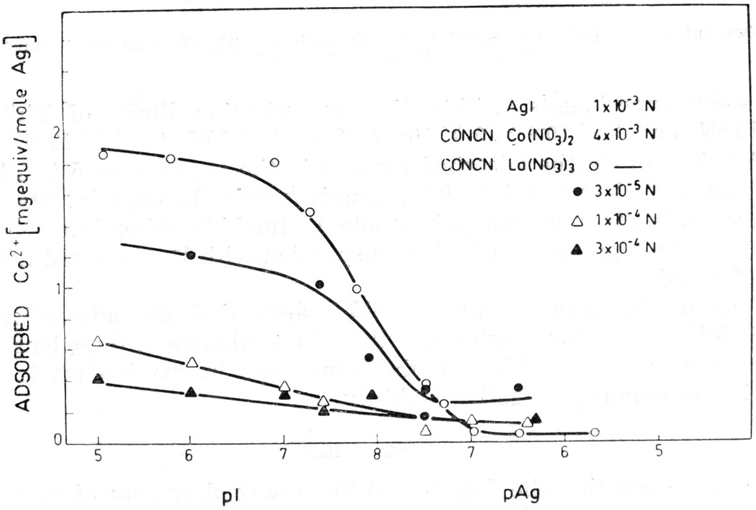

Fig. 8. Desorption of Co^{2+} by $La(NO_3)_3$ in dependence of pI. Constant concentration of $Co(NO_3)_2$ in solution: 4×10^{-3} N.

is given. This plot is a reproduction of the observation made earlier[1,2] that the adsorbed amount of an ion in the region of excess I^- ions is almost constant. The change in the adsorbed amount is confined practically into a maximum of two log. units, of activity of I^- between *p*I 7 to *p*Ag 7. The zero point of adsorption is equal to that found in experiments with Eu^{3+}, at *p*Ag 7.3

Desorption experiments of Co^{2+} with a second counter ion present were carried out with Th^{4+}, La^{3+}, Sr^{2+} and Na^+. All ions gave plots analogous to those given in Figs. 8 and 9 for La^{3+} and Sr^{2+}.

All these results indicate an invariable zero point of adsorption at *p*Ag 7.3, independent of the valency and the concentration of the adsorbed ion and of the valency and the concentration of the second counter ion present.

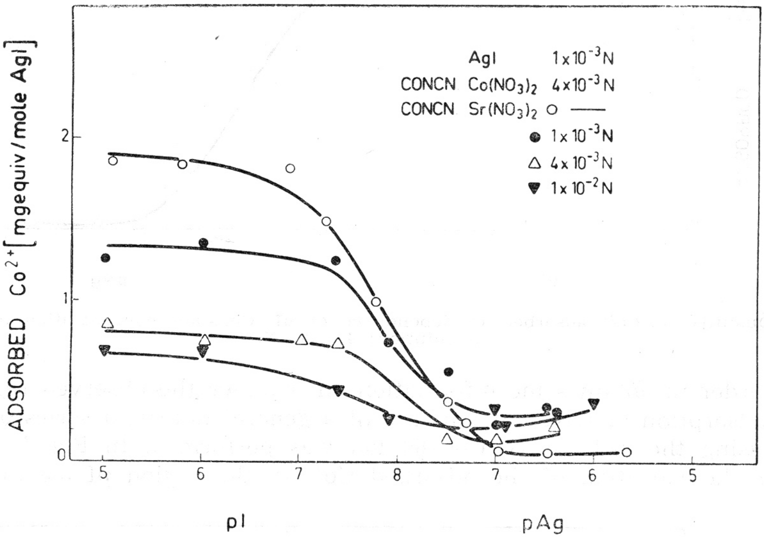

Fig. 9. Desorption of Co^{2+} by $Sr(NO_3)_2$ in dependence of *p*I. Constant concentration of $Co(NO_3)_2$ in solution: 4×10^{-3} *N*.

In some experiments, within the concentration limits of Th^{4+} 3×10^{-6} to $3 \times 10^{-5} N$, La^{3+} 3×10^{-5} to $3 \times 10^{-4} N$, Sr^{2+} 1×10^{-3} to $1 \times 10^{-2} N$ and Na^+ 1×10^{-2} to $3 \times 10^{-2} N$, the adsorbed amount in the region *p*Ag 5 to 7.3 was not zero but amounted from 0.1 to 0.3 mgequiv./gmole. In experiments with Eu^{3+} it was always less than 0.1 mgequiv/gmole. It should be taken into consideration that on titrating a positive AgI sol or suspension with I^- additional new surface may be formed.

Results of the experiments described show that the adsorption of Eu^{3+} and Co^{2+} follows the same rules and that the exchange of these ions with Th^{4+}, La^{3+}, Sr^{2+} and Na^+ are subject to the same laws in the isoelectric region as well as in the region of negative stability.

DISCUSSION

We can assume that the decrease of the adsorbed amount of counter ions is equal to the increase of the adsorbed amount of Ag^+ ions *i.e.* to the amount of Ag ions which entered the double layer and neutralized the excess adsorbed

I — ions. The amount of the adsorbed Ag ions can be computed from the difference between the value γ_{coag} and the adsorbed amount of Eu^{2+} counter ions.

From the results of Fig. 6 the plot »logarithm adsorbed amount of Ag^+ against *p*Ag" was constructed and given in Fig. 10. The intersection of the tangents on the plot with the pAg_{limit} ordinate was taken as the value of the total adsorbed amount of I — ions, γ_{stab}, in the stable region. The obtained value $\gamma_{stab} \cong 20$ mgeqeuiv./gmole AgI corresponds to the same value determined by the counter ion coagulation and adsorption (~ 20 at *p*I 3) in the preceeding paper[4]. In both cases the value γ_{stab} was about ten times higher than the γ_{coag}, and very close to the value 14 estimated from the potentiometric results on I^- ion adsorption of ref. 5. All plots shown are extensions of the plots »adsorbed quantity against *p*I« in the region $6 < pI$ to $pAg > 5$ reported in the preceeding papers[1,3,4] for the region $3 < pI < 6$.

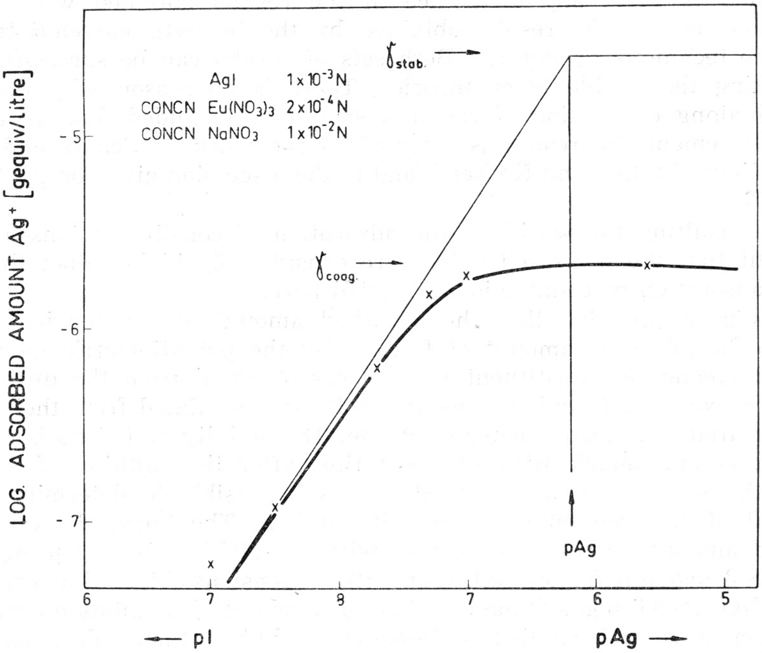

Fig. 10. Calculated quantity of Ag^+ adsorbed (= equivalent of Eu^{3+} desorbed) in dependence of *p*I. Calculation on the basis of results shown in Fig. 6.

The present results confirm the conclusion that the adsorbed amount of I^- ions per AgI particle may be considered constant in the whole region of the negative stability. This adsorption changes practically within two pI (*p*Ag) units and vanishes abruptly at *p*Ag 7.3. The presence of Ag^+ ions in excess is necessary to neutralize the adsorbed I^- ions. In the first group of figures (Figs. No. 1 to 5) the plots show an almost continuous change in the adsorbed amount with increasing *p*I. There is no horizontal part of the plots indicating a constant amonut of adsorbed counter ions. This is presumably due to the inadequacies in the experimental technique. These points were not measured on sols obtained by direct coagulation at the given *p*I value as were those in the preceding papers[1,2]. Except for the first point with the lowest *p*I value, all points were obtained by a gradual increase of the *p*I value caused by subsequent additions of $AgNO_3$ to the same sol, and after each addition the system was left to age for a given time to equilibrate.

The second group of the figures shown (Figs. 6—9) is however a direct confirmation of the transition from the nearly constant part in the region $3 < p\text{I} < 7$ to the steep decrease to zero at *p*Ag 7.3. The plots are an exponential asymptotic transition of the adsorbed amount with *p*I value within approximately 2 units from zero to the constant γ_{coag} value.

The results of the present investigations show that there is no difference in the zero point of the adsorbed amount on fresh, aged, and dried precipitates. This suggest that there is no basic difference between the mechanisms of adsorption operative on either the fine primary or on the coarse recrystallized particles.

Neither is there any difference in the results obtained with sols and suspensions nor in the results obtained by the *in statu nascendi* technique or by the technique of »aging«. Both sets of results can be successfully used in checking the double layer theories. There is no reason why the results obtained along either line of research should be excluded. For an aditional similar statement the reader is referred to the work of Schulz and Težak[16] and Matijević, Mathai and Kerker[17], and to the discussion given on pp. 224—226 of ref. 23.

By consulting the work[5] on the adsorption of constituent ions on AgI it is evident that the measured values are considerably higher than the values for the adsorption of counter ions reported here.

It is most probable that the adsorbed amount of counter ions will be equal to the adsorbed amount of I^- ions. By the potentiometric method[5] the adsorbed amount of constituent I^- ions was obtained from the difference of the added excess of I^- and the amount of I^- ions calculated from their activity and measured with an indicator electrode. The activity of I^- ions is measured during a potentiometric titration short time after the addition of $AgNO_3$ or NaI to the system. By this method it was impossible to determine directly the point of zero adsorption of constituent ions. The linear decrease of the adsorbed amount[5] per unit in pI was with the stable sols ($10^{-3}M$ AgI) much higher ($\simeq$ 3 mgequiv./gmole AgI) than with suspensions obtained by coagulation with $NaNO_3$ ($\simeq$ 0.6 mgequiv./gmole AgI). The adsorbed amounts on coagulated suspension were not studied systematically, but a linear decrease of the adsorbed amount with *p*I was observed with an approximate slope of 0.6 mgequiv./gmole AgI per *p*I unit. This value is of the same order of magnitude as the value 0.25 measured with counter ions. The difference of these values could be explained by the fact that the former value was obtained immediately after the activity change, while the latter after several tens of minutes. The higher value for the slope in stable sols, $\sim$ 3 mgequiv./gmole indicates that the amount adsorbed is larger here than in coagulated suspensions. The coagulation of sols by counter ions can be interpreted as the transition from the adsorbed amount γ_{stab} to the amount γ_{coag}. The isoelectric coagulation is accordingly a transition to zero adsorption.

The constancy of the total amount adsorbed of I^- ions with *p*I, and the relative ease with which the counter ions can be exchanged, suggest that the constituent ions may be assumed to be irreversibly adsorbed from $pI \sim 2$ up to pI 7. The counter ions are reversibly adsorbed following the elementary thermodynamic laws of ion exchange[11,12,18]. Since the absolute amount of the adsorbed ions is small (few ions per primary colloidal particle)[18] we may assume that the adsorbed electrolyte »counter ion — I^- ion« is fully dissociated and that the adsorbed amount γ is essentially equal to the charge σ on the particles. Probably only a minor, negligible part is associated to form neutral species in the layer. According to all theories of electrokinetic phenomena, the electrokinetic tension is proportional to the charge density and therefore the observed constancy of the electrokinetic tension with pI[20] is a logical consequence of the observed constancy of the adsorbed amount of counter ions with pI. A similar constancy with pI was observed[14,15] for the variation of the coagulation value with pI.

These observations prove that coagulation and electrokinetic phenomena are directly connected with adsorption processes in the double layer and not with oxidation-reduction processes. In addition a theoretical argument was brought forward[21] according to which the interpretation of tension on colloidal particles in terms of the reversible Nernst potential of electrochemical cells is not feasible.

In the extended version of the Derjaguin-Landau-Verwey-Overbeek theory put forward by Lyklema and Overbeek[20] the constancy of the electrokinetic tension was explained by a supposed variation of the value of the viscosity in the double layer. The double layer tension (the surface potential) was calculated by means of the Nernst equation from the excess concentrations of Ag^+ and I^- ions. This correction of the linear »surface potential against pAg ($-pI$)« relationship with a slope of RT/F is, however, superfluous, since in all heories the elektrokinetic tension is proportional to the charge density. The latter was shown to be constant with pI (pAg) by direct measurements.

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IZVOD

Određivanje adsorpcije iona metodom radioaktivnih indikatora. VI. Adsorpcija protuiona na srebrnom jodidu u području ekvivalencije.

D. Tesla-Tokmanovski, M. J. Herak, V. Pravdić i M. Mirnik

Mjerena je količina adsorbiranog Eu^{3+} i Co^{2+} na koaguliranom talogu srebrnoga jodida u području ekvivalencije od *p*J 5,5 do *p*Ag 5.5. Mjerenja su pokazala da je adsorbirana količina protuiona približno konstantna u području *p*J 5,5 do *p*J 7. Kod viših *p*J vrijednosti dolazi do postepene desorpcije protuiona i kod *p*Ag 7,3 adsorbirana količina je jednaka nuli u granicama eksperimentalne pogreške. Adsorbirana je količina osim toga neovisna o koncentraciji protuiona u otopini, ako je ista ravna koagulacionoj ili veća od nje. Ustanovljeno je da starenjem taloga, ili drugim vrstama predobrade, adsorbirana količina postaje manja, ali osnovne relacije koje određuju karakter adsorpcije se ne mijenjaju. Nizom eksperimenata ustanovljena je adsorpciono-desorpciona ravnoteža jednog adsorbiranog iona u prisutnosti nekog drugog iona u otopini.

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