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Adsorption of Thorium on Silver Halides and Silver Thiocyanate Sols

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The adsorption of thorium has been determined on freshly prepared, coagulated sols of silver halides and silver thiocyanate. The amount of adsorbed thorium has been measured radiometrically by addition of thorium-234.

It was found that the adsorption of thorium was much stronger on positively charged sols; on the negatively charged sols the adsorption was much less pronounced. The acidity also influences the adsorption, so that it is higher at greates *p*H values (measured up to *p*H = 4.5). The adsorption is nearly equal on coagulated sols of silver chloride, silver bromide and silver iodide; on silver thiocyanate is considerably less.

The presence of sulphate ion prevents the adsorption of thorium on negatively charged sols, and there is no effect on positive sols. The adsorption equilibrium was established in less than 5 minutes.

When the coagulation of lyphobic sols is carried out with neutral electrolyte solutions of highly charged counterions — especially with trivalent and tetravalent ions — usually the phenomenon of so called »irregular series« will be observed; instead of one coagulation region we have two regions. At high and low concentrations of electrolyte it comes to the coagulation, medial values on the contrary stabilize the sol. This phenomenon can be formally explained: if coagulation ions are strongly charged it is necessary to add only a litle amount of electrolyte to coagulate the sol. With slightly higher concentrations there will be no coagulation and the charge of the sol will be reversed. Only considerably higher concentrations of the electrolyte can coagulate again. And now the coagulating ion is no more the highly charged counter-ion but usually the lower charged accompanying ion. The mechanism of the reversal of the charge of the lyophobic sols is not yet quite explained.

Generally it is considered that the products of hydrolysis of these highly charged counter-ions are responsible for the phenomenon of the reversal of the charge[1]. This might prove the fact that the change of charge of sols will occur in neutral and alkaline solutions but not in strongly acid solutions. On the other hand it is certain that the mechanism of the reversal of the charge with multivalent ions differs from that with great monovalent ions, as are the inorganic complex ions and great organic ions. The thorium ion, as highly charged ion, is very convenient for studying the mechanism of the reversal of charge of negative sols and it was often used for this purpose. In the first place we were interested in the adsorption of thorium on coagulated sols of silver halides and silver thiocyanate hoping that by varying the conditions of the investigation some data could be obtained which will help to explain the action of thorium ions on these sols. The quantity of adsorbed thorium can be measured easily by adding the solutions radioactive thorium (Th-234).

EXPERIMENTAL

The systems investigated were prepared in the usual way[2] by mixing 5 ml. of $AgNO_3$ solution with 5 ml. of a solution which contained the halogen component and $NaNO_3$ or Na_2SO_4. The solution of $Th(NO_3)_4$ were added to the solution of precipitating component in excess which contained also radioactive Th-234 isolated in a very simple way from $UO_2(NO_3)_2$ as described by Dyrssen[3].

To be able to separate the solid phase from the solution it was necessary to work in the coagulating region, and for this reason we added the necessary amount of $NaNO_3$ and Na_2SO_4 respectively. The precipitate was separated from the solution by centrifuging it and the activities were measured in the aliquot volume of the solutions. The counting was performed by a G.-M. counter (made in Institute »Ruđer Bošković«). A strong linear function between the concentration of thorium and counted numebr of impulses was obtained. The activity of the systems was always determined against the standard solutions. These standard solutions were made without adding one of the precipitating components (silver nitrate or potassium or sodium halide). When silver was in excess we did not add the halide component and when the halide was in excess silver nitrate was not added. The acctivities were measured half an hour after preparing the systems and after 24 hours. Generally there was no difference in activities between these two readings.

RESULTS

On Fig. 1 the results are shown with the systems: $KI—AgNO_3—Th(NO_3)_4—NaNO_3$ and $KI—AgNO_3—Th(NO_3)_4—K_2SO_4$. The results were in a way unexpected. The adsorption of thorium (final concentration in solution was 1×10^{-6} *N*) was stronger on positively charged sols than on negatively charged sols. The adsorption increased with excess of Ag^+ ions, so that at an excess of 0.039 *M* nearly 100% of the added amount of thorium was adsorbed. At negatively charged sols, where we may expect a greater adsorption, it was significantly lower. There was also a great influence of the accompanying ion on the negative sols. In the presence of sulphate ions there were no adsorption at all. On the positive side there was no difference in adsorption.

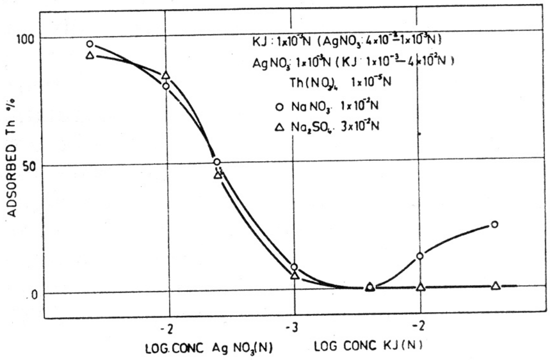

Fig. 1. Adsorption of thorium on freshly coagulated sols of silver iodide in presence of 0.01 *N* $NaNO_3$ and 0.03 *N* Na_2SO_4 respectively. The concentration of AgI was 0.001 *M* and the concentration of Th in the systems was 1×10^{-5} *N*.

Because of the great influence of acidity on the precipitation of silver halides in presence of thorium[4] we also measured the adsorption at different *p*H. The results are shown on Fig. 2. The higher the *p*H the greater the adsorption on positive sols, and at *p*H = 4 the adsorption was nearly 100% with respect to the amount of thorium. On the negatively charged sols we found the adsorption of thorium only at *p*H higher than 3. In the presence of sulphate

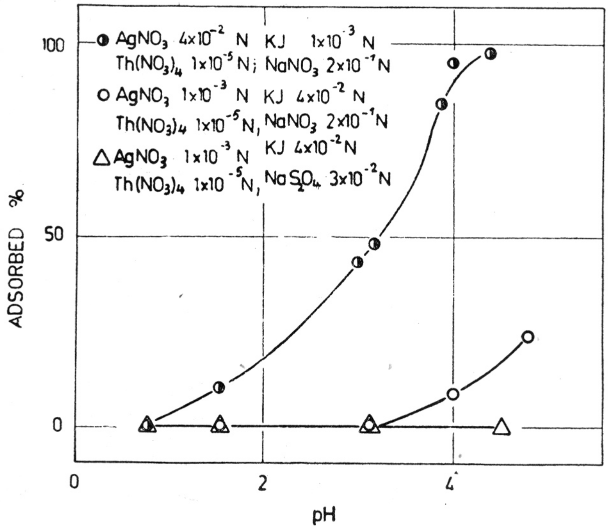

Fig. 2. Influence of *p*H on the adsorption of thorium on freshly coagulated sols of silver iodide in presence of 0.01 *N* $NaNO_3$ and 0.03 *N* Na_2SO_4 respectively. The concentration of AgI was 0.001 *M* and the excess of Ag^+ or I^- was 0.039 *N*.

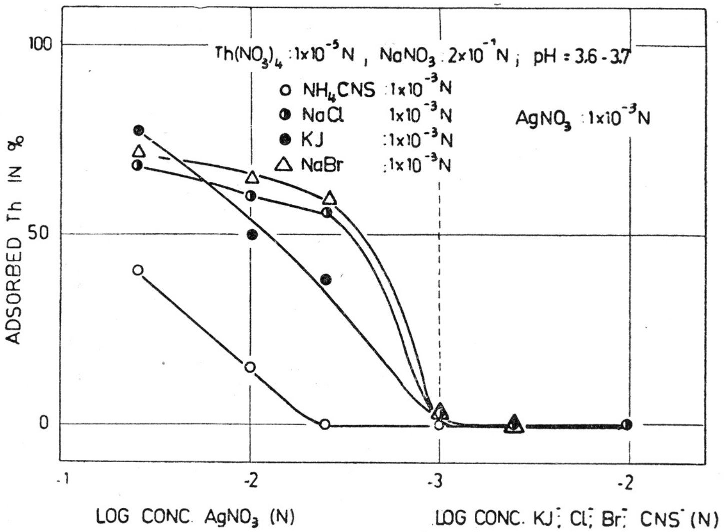

Fig. 3. Determination of the adsorption of thorium on coagulated sols of AgCl, AgBr, AgI, and AgSCN respectively. The concentration of added $NaNO_3$ was 0,2 *N*. The amount of solid phase was 0.001 *M* and the concentration of thorium in the systems 1×10^{-5} *N*.

ion there was no adsorption, regardless of the *p*H. The measurements were carried out at the *p*H values lower than 4.5; at the higher there is a significant precipitation of thorium because of hydrolysis (see e. g.[5]). We varied the *p*H by addition of nitric acid and measured it on a Beckman *p*H-meter with a glass electrode.

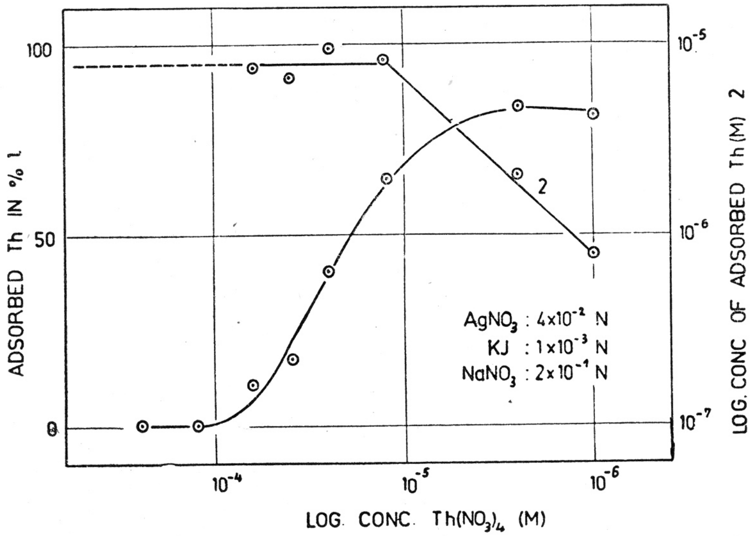

Fig. 4. Dependence of the adsorption of thorium on its concentration in solution. The concentration of AgI was 0.001 *M* with an excess of Ag^+ 0.039 *N*.

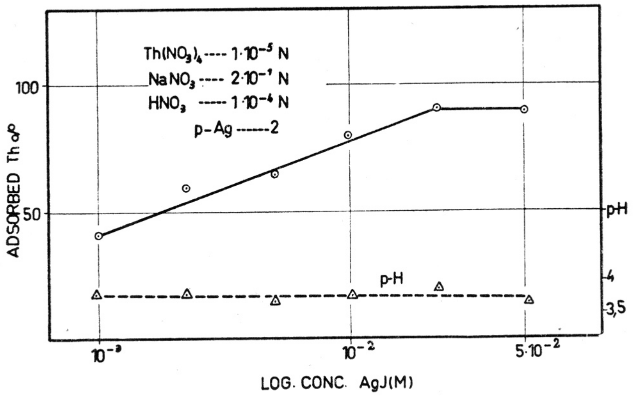

Fig. 5. Dependence of the adsorption of thorium on the amount of solid phase. The AgI sols were prepared with an excess of Ag^+ 0.01 *N* in presence of 0.2 *N* of $NaNO_3$. The concentration of thorium in the systems was 1×10^{-5} *N*.

The comparison of the adsorption of thorium for different coagulated silver halide sols and silver thiocyanate sols was also interesting, as can be seen on Fig. 3. When the halide or thiocyanate component was in excess there was no adsorption under experimental conditions. When silver was added in excess the adsorption of thorium was nearly equal at AgCl and AgBr sols; the adsorption curve for AgI sols differs slightly from the curves for AgCl and AgBr sols. The adsorption on AgSCN sols is lower and begins at a greater amount of Ag^+ ions, *i.e.* at higher positively charged sols.

The dependency of the adsorption on the concentration of thorium is given on Fig. 4. The sol was positive and its concentration was 0.001 *M* with an excess of 0.039 *M* $AgNO_3$ and was coagulated with $NaNO_3$ (final concentration 0.2 *N*). As we expected the amount of adsorbed thorium increases with its concentration. The adsorption is constant at nearly 1×10^{-5} *N* of Th and amounts to 8×10^{-6} moles/l. when the quantity of the solid phase is 0.001 moles. At the concentrations of thorium larger than 0.0001 *M* the adsorbed should be determined on the precipitate and not in the solution. The concentration of thorium in the solution is in excess and therefore very little changed by adsorption. The precipitate should be completely freed from the solution. In this separation the change of adsorption equilibrium might take place.

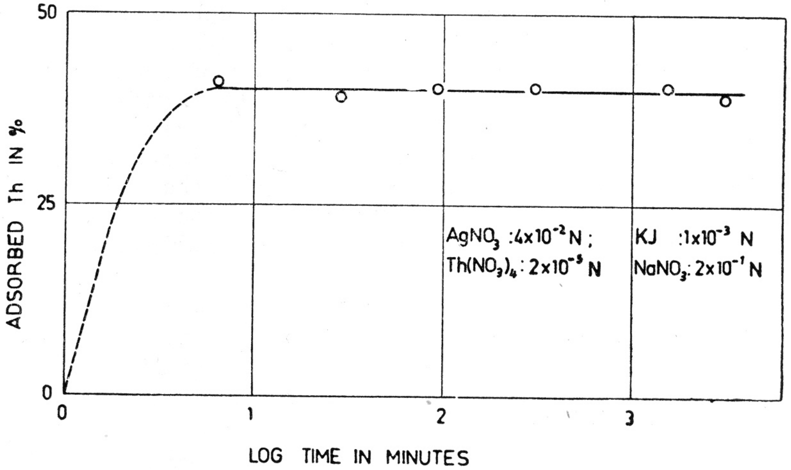

Fig. 6. Adsorption of thorium as a function of time. AgI was precipitated with an excess of Ag^+ 0.039 *N* and in the presence of 0.2 *N* $NaNO_3$. The concentration of thorium in the systems was 2×10^{-5} *N*.

When the quantity of the solid phase at a constant excess of Ag^+ ($pAg=2$) and a constant *p*H of 3.75 was varried the quantity of the adsorbed thorium increased and became steady at 0.022 *M* AgI.

In alll our systems the adsorption equilibrium was established in rather short time, after 5 minutes or even earlier (Fig. 6). The exact time we could not determine since we needed 5 minutes to prepare the systems for measurement.

DISCUSSION

As we mentioned before the results were in a way surprising. We expected the adsorption of the positively charged thorium ion or its complex ion to be much stronger when sols are negatively charged, but it was not so. This phenomenon is now difficult to explain. On the positively charged sols the adsorption is the greater the more positively charged the sols are, *i. e.* the greater is the excess of the stabilizing ion.

At negatively charged sols the adsorption is less pronounced but it depends on the agents which influence the reversal of the charge: they are primarily the *p*H and the accompanying ion. The adsorption is greater at higher *p*H values; when the $pH < 1$ there is no adsorption either on the positively or the negatively charged sols. The adsorption reaches its maximum at *p*H approximately equal to 4. This may indicate that the adsorption is connected with the formation of complex thorium ions. At still higher *p*H values the products of hydrolysis of thorium precipitate and we cannot measure the adsorption. The influence of *p*H is in accordance with the proposed mechanism for the reversal of the charge of highly charged ions. In strongly acid solutions positively charged complex products are not formed and the negative sols will not change the charge. In this *p*H region there is no adsorption.

The influence of sulphate ions is very interesting. In presence of sulphate ions there is no adsorption of thorium on negative silver halide sols. On the positively charged sols there is no influence of the sulphate ion on the adsorption. It is evident that the adsorption mechanism on positive sols differs from the mechanism of the negative sols. This influence of sulphate ion may be distinctly seen at the reversal of the charge on the negative silver halide sols with thorium. To accomplish the reversal of the charge in a sulphate medium we need much higher concentration of thorium, about 0.01 *N*. In the presence of nitrate ion the charge of the sol is changed by addition of 8×10^{-5} *N* of thorium[4]. This effect of the sulphate ion probably could be explained in this way that thorium builds sufficient stable complex $Th(SO_4)_2$; the nitrate complexes are less stable[6].

In spite of the difference in the charge densities on the silver halide sols (which is increasing from AgCl to AgI), it is not especially pronounced at the adsorption of thorium. The exception is only the thiocyanate ion because the character of this ion differs from that of halide ions.

The results show that the adsorption of thorium and related phenomena, as *e. g.* the reversal of the charge of sols, are complicated processes which are influenced by many factors. Some of these influences are not yet clear and therefore could not be explained.

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IZVOD

Adsorpcija torija na solovima argentum halogenida i argentum tiocijanata

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Adsorpcija torija bila je određivana kod svježe priređenih, koaguliranih solova argentum halogenida i argentum tiocijanata. Količina adsorbiranog torija bila je mjerena radiometrijski dodatkom Th-234.

Nađeno je, da je adsorpcija torija mnogo jača na pozitivno nabijenim solovima; na negativno nabijenim solovima ona je znatno slabija. Na adsorpciju utječe i aciditet, tako da je adsorpcija veća kod viših *p*H vrijednosti (mjereno do *p*H = 4.5). Adsorpcija je gotovo jednaka na koaguliranim solovima argentum klorida, argentum bromida i argentum jodida; znatno je slabije izražena na solovima argentum tiocijanata.

Nazočnost sulfatnog iona potpuno sprečava adsorpciju torija na negativno nabijenim solovima, a bez efekta je kod pozitivno nabijenih solova. Adsorpciona ravnoteža uspostavlja se u vremenu kraćem od 5 min.

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