

969. *The Adsorption of Cations at the Silver Iodide-Solution Interface. Part II.¹ Thorium.*

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The adsorption of thorium on silver iodide powder has been measured as a function of pH, by use of ²³⁴Th as a tracer. The isotherms appear to be of the Freundlich type. The extent of adsorption increased with pH, gradually between 2.0 and 4.2, and very rapidly above 4.2. The results indicate that simple hydrolysis products may be the adsorbing species below pH 4.2, but above this adsorption of multinuclear complexes occurs. These conclusions are supported by electrokinetic measurements.

PREVIOUS work indicated that the variation of the flocculation concentration of thorium with pH, such as occurs with silver iodide sols, can be attributed to variation of the extent of adsorption of thorium at the solid-liquid interface with pH.² The latter effect appears to arise as a consequence of hydrolysis of the thorium ion in solution as the pH is increased. Some preliminary adsorption measurements using sol particles were not sufficiently precise for a detailed interpretation to be made.³ In the present work the adsorption of thorium in suspensions of silver iodide of known surface area has been examined in detail as a function of pH, ionic strength, and temperature. The results, combined with electrokinetic measurements, enable some conclusions to be reached about the change in nature of the adsorbing thorium species with increase of pH.

EXPERIMENTAL

Materials.—The materials and procedures were the same as those used previously,¹ except where otherwise stated. Thorium nitrate and uranyl nitrate were B.D.H. AnalaR material. Stock thorium nitrate solutions were made up in dilute nitric acid (pH *ca.* 2.5) to reduce the "ageing" which takes place in solutions of higher pH.

Preparation of Thorium-234.—The isotope was isolated from uranyl nitrate by use of the procedure suggested by Dryssen.⁴ Zeo-Karb 225, however, was used for the preparation of the ion-exchange column. The ²³⁴Th was eluted from the column as the oxalate, and this was decomposed to the oxide which was dissolved in concentrated nitric acid and evaporated to dryness. A stock solution of ²³⁴Th was made (*ca.* 10⁻⁸M) by dissolving the thorium nitrate in 10⁻³M-nitric acid. The half-life of the ²³⁴Th was found to be 24.3 days, in good agreement with literature values.

The results for the adsorption of thorium on glass, as a function of pH, were substantially the same as those of Rydberg and Rydberg.⁵

RESULTS

Adsorption.—The results obtained for the adsorption of thorium on silver iodide powder at pI 4 in 10⁻³M-sodium nitrate, at five pH values in the range 2—5.2, are presented in Fig. 1. Although there is a spread in the results the curves at each pH appear to be linear. Some of the spread in results was probably due to the difficulty in adjusting the pH precisely without a buffered system; buffer ions, however, are usually organic ions or multivalent ions, and were excluded from the system owing to their tendency to be strongly adsorbed. The curve at pH 5.2 was the most difficult to obtain, and therefore has the greatest scatter; in this region incipient formation of colloidal thorium hydroxide occurred. The data in Fig. 1 appear to fit Freundlich isotherms of the form, $\log x = \log k + (1/n) \log c$, where x = number of moles of thorium adsorbed per gram of silver iodide, c = equilibrium concentration of thorium, and k

¹ Part I, Abramson, Jaycock, and Ottewill, preceding Paper.

² Matijević, Abramson, Schulz, and Kerker, *J. Phys. Chem.*, 1960, **64**, 1157.

³ Matijević, Abramson, Ottewill, Schulz, and Kerker, *J. Phys. Chem.*, 1961, **65**, 1724.

⁴ Dryssen, *Svensk kem. Tidsskr.*, 1950, **62**, 153.

⁵ Rydberg and Rydberg, *Svensk kem. Tidsskr.*, 1952, **64**, 200.

and n are constants. The isotherms at pH 2.0, 2.6, and 3.1 as drawn, are represented by the following equations:

$$\text{pH } 2.0, \log x = -5.19 + 0.37 \log c;$$

$$\text{pH } 2.6, \log x = -4.86 + 0.40 \log c;$$

$$\text{pH } 3.1, \log x = -4.66 + 0.43 \log c.$$

An attempt was also made to measure the variation of the adsorption with temperature. However, within the limits of experimental error the results were not distinguishable from those obtained at room temperature. Similarly, increasing the concentration of sodium nitrate from 10^{-3}M to 10^{-1}M did not produce any significant difference in the results.

A few experiments were also carried out in 10^{-3}M -sodium nitrate at pAg 3 and pH values of

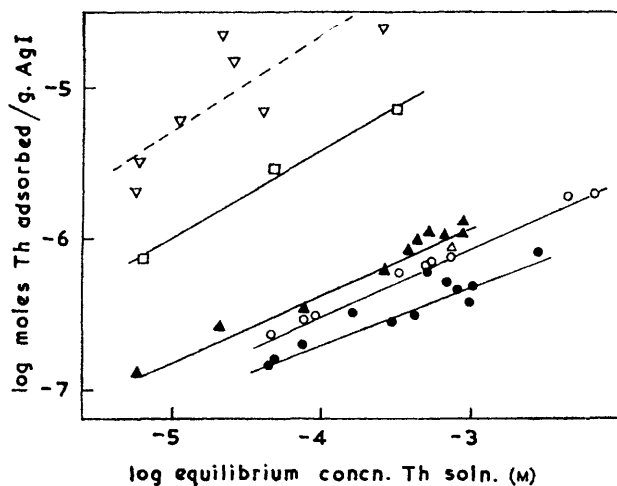


FIG. 1. Variation of the number of moles of thorium adsorbed with the equilibrium concentration of thorium nitrate, in a solution 10^{-3}M in sodium nitrate and 10^{-4}M in potassium iodide (pH adjusted with nitric acid).

pH (± 0.1): ●, 2.0; ○, 2.6; ▲, 3.1; □, 4.3; ▽, 5.2.

1.9 and 3.6. Adsorption of thorium on the positively charged surface was observed and this increased with increasing pH. These findings corroborate the results of Schulz and Herak.⁶

Some experiments on desorption indicated that desorption did occur but the rate was slow. The adsorption, moreover, appeared to be largely determined by the pH of the thorium nitrate solution when the silver iodide powder was added. Lowering of the pH of the system, after adsorption, did not necessarily appear to return the system to the conditions expected for the isotherm determined at the lower pH. Probably, this behaviour can be attributed to the slow rate of the desorption process.

Microelectrophoresis Measurements.—The experiments were divided into two groups, those carried out as a function of thorium concentration at constant pH, and those carried out at a constant thorium concentration as a function of pH.

The results of the experiments with thorium nitrate are given in Fig. 2. In 10^{-4}M -thorium nitrate the mobility increased steadily from $0.6 \mu/\text{sec.}/\text{V}/\text{cm.}$, at pH *ca.* 2.1, to 3.15 at pH *ca.* 3.8. A rapid increase of mobility then occurred up to a maximum of 4.9 at pH 4.2; beyond this it fell off rapidly until at pH *ca.* 6 measurements became very difficult owing to the precipitation of thorium hydroxide. The curve in 10^{-3}M -thorium nitrate was very similar except that the mobilities were in general slightly higher and the maximum was reached at pH 3.8.

The variation of zeta-potential with concentration of thorium nitrate for a silver iodide suspension at pI 4 in 10^{-3}M -sodium nitrate solution is shown in Fig. 3. The zeta-potentials were calculated by use of the formula of Overbeek.⁷ The shift of the zero-point of charge did

⁶ Schulz and Herak, *Croat. Chem. Acta*, 1958, **30**, 127.

⁷ Overbeek, *Kolloid-Beih.*, 1943, **54**, 287.

not appear as pronounced with the suspensions as it was with the sols used in previous work.³ Moreover, owing to the nature of the suspensions the precision was not as good as with the sols. It is of interest, however, that at the same pH the zero point of charge of the suspensions is found at a higher thorium nitrate concentration than with the sols (cf. ref. 3).

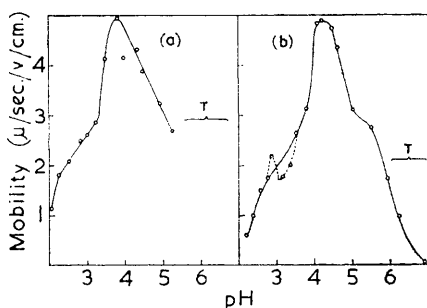


FIG. 2. Variation of electrophoretic mobility of silver iodide particles with pH, at constant thorium nitrate concentration: (a) 10^{-3} M; (b) 10^{-4} M. Thorium hydroxide was precipitated in the region T.

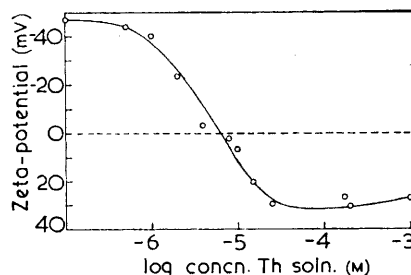
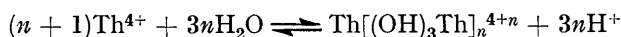


FIG. 3. Variation of the zeta-potential of silver iodide particles with concentration of thorium nitrate at pH 3.1.

DISCUSSION

Adsorption.—The hydrolysis of the thorium ion in solution is clearly a complicated process and not at present completely elucidated.^{8,9} The technique most used so far to study this phenomenon, has been the electrometric titration of thorium salts in solutions of high ionic strength. Heitonen and Sillén¹⁰ express the hydrolysis as a general reaction by the equation



with an equilibrium constant of $10^{-7.5}$ for $n = 1$. Their results appear to agree well with those of other workers, *e.g.*, Krauss and Holmberg.¹¹ In a recent study Bilinski, Füredi, Branica, and Težak¹² found that highly hydrolysed multinuclear thorium ion species are predominant in the solution above pH 4.1.

On the basis of coagulation studies carried out *in statu nascendi*² it has been suggested that the initial hydrolysis step produces $[\text{Th}(\text{H}_2\text{O})_{x-1}\text{OH}]^{3+}$ whilst at higher pH a dimer is formed, $[\text{Th}(\text{H}_2\text{O})_{x-1}\text{OH}]_2^{6+}$. Undoubtedly coagulation provides a sensitive means of detecting hydrolysis of ions in solution but in the light of the present adsorption studies it would appear unlikely that the determination of the charge of the hydrolysed species by this method is a simple matter. Moreover, the application of the Schulze-Hardy rule under conditions where adsorption of the counter-ion species occurs, must be questioned.

The adsorption isotherms (Fig. 1) show that as the pH is increased from 2.1 to 5.2 there is a steady increase in the adsorption of thorium. This is shown more clearly in Fig. 4 where log moles of thorium adsorbed is plotted against pH for constant equilibrium thorium nitrate concentrations of 10^{-5} , 10^{-4} , and 10^{-3} M. Although there is a gradual increase between pH 2 and 3, the main onset of adsorption occurs above pH 3. Just above pH 5 the amount adsorbed is nearly one hundred times that at pH 2.

⁸ Sillén, *Quart. Rev.*, 1959, **13**, 146.

⁹ Hietanen and Sillén, *Acta Chem. Scand.*, 1954, **8**, 1626.

¹⁰ Hietanen and Sillén, *Acta Chem. Scand.*, 1959, **13**, 533.

¹¹ Krauss and Holmberg, *J. Phys. Chem.*, 1954, **58**, 325.

¹² Bilinski, Füredi, Branica, and Težak, *Croat. Chem. Acta*, 1963, **35**, 19.

Comparison of the curves of pH against mobility at constant thorium nitrate concentration (Fig. 2) with the corresponding adsorption curve in Fig. 4 shows that, although the mobility goes through a maximum, the adsorption continues to increase. In Fig. 5 the ratio of the number of moles of thorium adsorbed per gram of silver iodide to the mobility of silver iodide is plotted as a function of pH for 10^{-4}M -thorium nitrate. On a simple basis, in the case of adsorption of a constantly charged species, at constant concentration of the ion, the ratio would be expected to remain sensibly constant with pH. This, in fact, occurs in the region below pH 3.1, but above this pH there is a marked increase in the ratio. In the pH region 3.1–4.2, the increase is gradual and would not be inconsistent with the adsorption of simple hydrolysed species of the type $\text{Th}(\text{OH})^{3+}$, $\text{Th}(\text{OH})_2^{2+}$, etc. Above pH 4.2, however, the pH at which the maximum occurs on the curve of mobility against pH, the ratio increases very rapidly. In view of the lowering of the mobility it

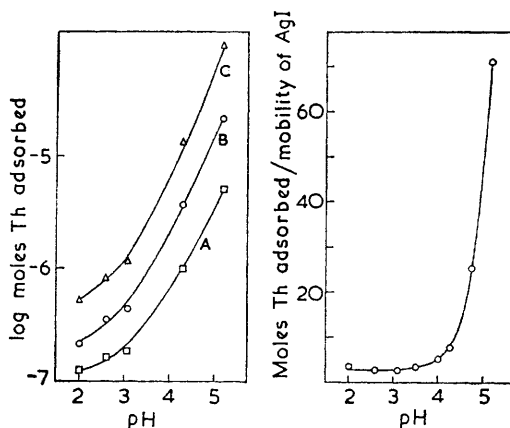


FIG. 4.

FIG. 5.

FIG. 4. Variation of moles of thorium adsorbed per gram of silver iodide with pH, at constant thorium nitrate concentrations: A, 10^{-5}M ; B, 10^{-4}M ; C, 10^{-3}M .

FIG. 5. Variation of the ratio of the number of moles of thorium adsorbed per gram of silver iodide to the electrophoretic mobility with pH, at a constant concentration of 10^{-4}M -thorium nitrate.

appears unlikely that the large amounts of thorium adsorbed could all be adsorbed with a charge of +3 or even +2 per thorium atom. This suggests either, that the thorium is adsorbed as a multinuclear complex with a low net charge per thorium, or, that the adsorbed layer is composed of neutral thorium hydroxide together with some hydrolysed ions. The former conclusion would be in agreement with the results of Bilinski *et al.*¹²

At pH greater than 6 the silver iodide particles were observed, under the ultramicroscope, to be held at a fixed distance from each other in small clusters, with diaphanous material between the particles. This material was almost certainly thorium hydroxide, and suggests that the lowering of mobility between 4.2 and 6 is due to the surface nucleation of the hydroxide. As intermediates in the formation of thorium hydroxide a whole series of multinuclear complexes must be formed, having the structural form of inorganic polymer chains.¹² It is possible that these nucleate and are adsorbed more strongly on the surface of the silver iodide than the simpler ion species.

Comparison of Electrokinetic and Adsorption Data.—In work on the adsorption of neodymium and lanthanum ions on silver iodide powder¹ it was found that, although both of these ions were adsorbed on silver iodide, the zeta-potential remained negative provided that the pH was maintained below 6. With thorium, however, as is well known,

reversal of sign of the zeta-potential occurs at very low concentrations of thorium nitrate.^{13,14} In the present work reversal of charge at pH 3.1 occurred at 6.6×10^{-6} M-thorium nitrate, and it can be calculated from the adsorption isotherm that this corresponds to one thorium ion adsorbed per 580 Å.

A comparison of the surface-charge density, calculated on the basis of the amount of thorium adsorbed, with that calculated from the electrokinetic potential showed the same divergence between the two curves as was found with lanthanum and neodymium. The curve calculated from direct adsorption measurements increased with increasing concentration much more rapidly than that calculated from electrokinetic data. At 10^{-4} M-thorium nitrate the adsorption value was about sixteen times the electrokinetic value, taking the valency of the adsorbed thorium species as 4.

Reversal of charge of the silver iodide surface was found at pH values below that at which hydrolysis of thorium can be detected by electrometric measurements carried out at high ionic strengths.⁹⁻¹¹ However, studies on the influence of thorium on the surface characteristics of myristic acid monolayers¹⁵ have indicated that hydrolysis can be detected by this technique at pH values considerably below those at which it is observed by electrometric measurements. It appears probable that even at pH 3 small amounts of hydrolysis products are present, and that it is these which are preferentially adsorbed at the silver iodide surface. This conclusion is substantiated by the increase in adsorption which occurs as the pH is raised from 2.0 to 3.1 (Fig. 1). It appears reasonable to conclude that the reversal of charge which occurs with thorium, and with lanthanum and neodymium at pH values between 6.2 and 8.3, can be attributed to the adsorption of ion hydrolysis products. The aluminium ion also fails to reverse the charge of negative silver iodide surfaces until hydrolysis of the ion has occurred.¹⁶

After hydrolysis of the ion, strong specific adsorption of the cation occurs at the interface, thus bringing an array of positive charges into the proximity of the plane of shear. Prior to hydrolysis the cation has little tendency to specific adsorption,¹⁷ and the charge in the electrokinetic plane remains net negative. With increasing extent of hydrolysis, *i.e.*, with increasing pH, the charge per thorium atom is reduced, and although the extent of adsorption is increased the reversal of charge concentration moves to higher values. Eventually, formation of negatively charged thorium hydroxide occurs and little effect is observed on the mobility of the silver iodide particles owing to the mutual repulsion between the two species.

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¹³ Abramson, "Electrokinetic Phenomena," The Chemical Catalogue Co., New York, 1934.

¹⁴ Kruyt, "Colloid Science," Vol. 1, Elsevier, Amsterdam, 1952.

¹⁵ Ottewill and Abramson, *J. Colloid Sci.*, 1962, **17**, 883.

¹⁶ Matijević, Mathai, Ottewill, and Kerker, *J. Phys. Chem.*, 1961, **65**, 826.

¹⁷ Grahame, *Chem. Rev.*, 1947, **41**, 441.