ACTINIUM: RADIOCOLLOIDAL BEHAVIOUR

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A number of heavy element hydroxides and sulphides are known to exhibit radiocolloidal properties[1]. Although many lanthanides have these properties[2,3], the existence of actinium hydroxide or sulphide as a radiocolloid does not appear to have been reported. During the course of extraction and separation of MsTh-1 and MsTh-2, it was found that the hydroxide of the latter formed a radiocolloid in solutions of high pH.

In addition to the usual methods of investigating radiocolloids, a paper chromatographic technique has been developed for the study of these colloidal systems. The method is based on the principle that a colloid when adsorbed on chromatography paper does not move with the eluant, while the ionic form does. The colloid formation can be readily studied by this method.

EXPERIMENTAL

MsTh-1 was separated from 2 kg of thorium nitrate by coprecipitating it with barium sulphate. The sulphates were fused with sodium carbonate and the fused mass was extracted with water and filtered. The residue was dissolved in the minimum amount of hydrochloric acid.

The radioactivity was assayed with the help of a scintillation counting set-up with a NaI(Tl) well-type crystal, and that on the paper strip was determined with the Tracer-lab TGC.2 GM counter in conjunction with a scaler.

(a) *Adsorption of MsTh-2 on sintered glass at various pH values*

1 ml of the original solution containing MsTh-1 in equilibrium with MsTh-2 was diluted to 10 ml and the pH adjusted to the desired value by the addition of ammonium hydroxide. This solution was immediately filtered through a sintered glass funnel under suction and washed with 5 ml of water adjusted to the same pH. This operation took less than three minutes. The matter asdorbed on the sintered glass was removed by washing it with 5 ml of concentrated nitric acid, which completely removed the adsorbed matter, as no activity was detected in further washings. The samples at different pH values were counted for a week and MsTh-2 estimated in each sample. The results are shown in Fig. 1.

The coagulation isotherm at pH 9.5 is obtained by determining the percentage adsorption at different concentrations of MsTh-2 and plotting the logarithm of the amount adsorbed *versus* the logarithm of the initial concentration. The results are given in Table I and are plotted in Fig. 2.

In order to study the effect of foreign electrolytes on the adsorption of MsTh-2 on sintered glass, increasing concentrations of KCl were used and the adsorption of MsTh-2 was determined at pH 9.5. The data are presented in Table II.

The effect of aging of the solutions on the adsorption behaviour of MsTh-2 was determined as follows:

1 ml of the original solution diluted to 10 ml was adjusted to the desired pH. The solution was then transferred to 20 ml glass-stoppered pyrex bottles and allowed to age for a desired length of time. Two series of experiments were conducted with aging times of 50 and 120 hours. The adsorption and elution from sintered glass was carried out as described above and the samples were followed for 3 to 4 days to obtain equilibrium values. Curves 2 and 3 in Fig. 1, refer to solutions aged for 50 and 120 hours respectively.

(*b*) *Centrifugation studies on the radiocolloid*

In each of five centrifuge tubes 5 ml of the MsTh-2 solution, adjusted to a definite pH value, was placed and then centrifuged for over 2 hours at 4000 r.p.m. The tubes were removed without disturbing the solutions. 3 ml of the solution from the top were very carefully removed to a vial and counted. The remaining solution was transferred to another vial along with the 2 ml of conc. HCl used for rinsing the centrifuge tube, and then counted. The results are given in Table III.

(*c*) *Paper chromatographic experiments*

The behaviour of a known radiocolloid, UX_1, on paper chromatography was first studied. A drop of a solution of uranyl nitrate in equilibrium with UX_1 was applied at one end of a paper strip and chromatographed with water at pH 3. A clear separation of UX_1 from uranium was achieved. UX_1, which forms a radiocolloid, does not move while the uranyl ions move along with the water front as verified by means of ferrocyanide solution. Similar studies with MsTh-2 have been carried out. 1 ml of the original solution was diluted to 10 ml and the pH adjusted to the desired value. 0.5 ml of this solution was applied with a micro-pipette to a strip of Whatman No. 3 MM paper and eluted with water adjusted to the same pH as the test solution. The results, plotted in Figs. 3–6, are discussed below.

RESULTS AND DISCUSSION

The original solution contains MsTh-1 and MsTh-2 in equilibrium. The radioactivity detected either by scintillation or with the GM counter is mainly due to the presence of MsTh-2, since MsTh-1 emits only weak β and γ rays. MsTh-2 is assayed by following its decay or growth in the solutions.

Curve 1 in Fig. 1 gives the plot of pH against the percentage adsorption of MsTh-2 on the sintered glass, when the solutions are filtered immediately after adjusting the pH. There is no significant adsorption up to pH 5, after which there is a sharp increase in adsorption. This adsorption continues to rise with the pH till a limiting value of 75 % is reached at pH 9.5.

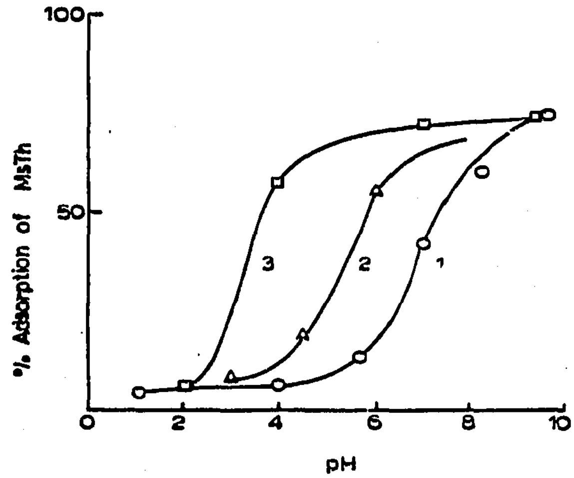

Fig. 1. Adsorption of MsTh-2 on sintered glass as a function of pH and time. Curve 1: zero hour; Curve 2: 50 hours; Curve 3: 120 hours.

When the solutions are aged, the curve shifts to the left, the shift being greater the longer the period of aging as indicated in curves 2 and 3 in Fig. 1, for 50 and 120 hours aging time respectively. This aging effect, however, cannot be interpreted in the same way as proposed by KURBATOV AND KURBATOV[4-6] and BOUISSIÈRES *et al.*[7] for the radiocolloidal formation of Y, Zr, Th and Ba in trace quantities. The mean life of MsTh-2 atoms in the solution is 8.86 hours, and so aging of its solutions for periods greater than 40 to 50 hours cannot be expected to have any effect on its adsorption behaviour. It is, therefore, surprising to find that an aging period greater than 50 hours (curve 3, Fig. 1) does influence the adsorption of MsTh-2.

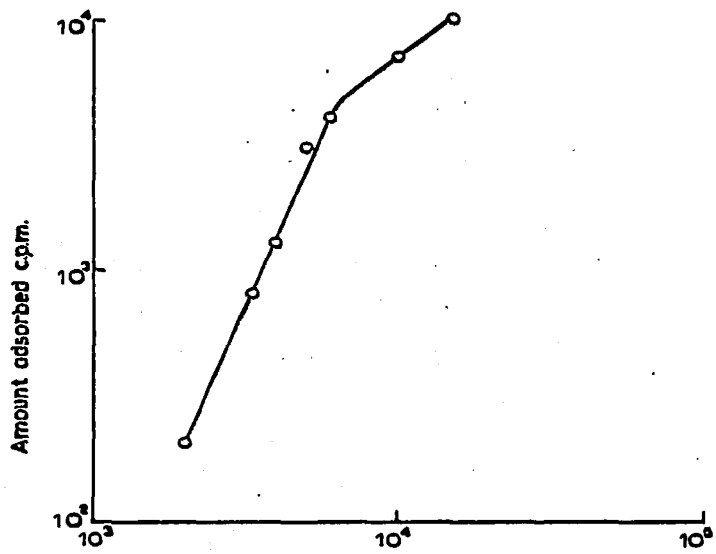

Fig. 2. Coagulation isotherm of MsTh-2 at pH 9.5.

The adsorption isotherm of MsTh-2 on sintered glass at pH 9.5, given in Fig. 2, shows that the percentage adsorption increases with the concentration becoming constant at higher concentrations of MsTh-2 (see also Table I).

TABLE I

ADSORPTION OF MsTh-2 ON SINTERED GLASS
(pH 9.5; volume of solution 10 ml)

Initial concentration c.p.m.	*Amount adsorbed c.p.m.*	*% adsorption*
2,000	211	10.5
3,300	810	24.6
4,000	1,300	32.5
5,000	3,106	62.0
6,000	4,140	69.0
10,000	7,200	72.0
15,000	10,780	71.49

The effect of concentration on the adsorption of radiocolloids on filter paper has been studied by KURBATOV *et al.*[4,5,8,9] for zirconium and thorium. They observed an increase in the adsorption with decreasing concentration of these substances, other variables remaining constant. However, in all these cases the concentration range lay between 10^{-6} and 10^{-12} g.atoms/l, whereas in our studies still lower concentrations were used. It appears from the results that in the case of MsTh-2, the (maximum) limit for the percentage adsorption is reached at concentrations as low as 10^{-12} g.atoms/l.

No variation in the adsorption of MsTh-2 on sintered glass was observed in the presence of varying amounts of KCl, although KCl was added up to an overall concentration of 0.5 *M*, as shown in Table II.

The decrease in the adsorption of zirconium and thorium reported by KURBATOV and others[4,5,8,9] was observed in the presence of a maximum concentration of 0.05 *M* KCl. The solutions of MsTh-2 used in the present series of experiments, contained comparable amounts of $BaCl_2$ (*vide infra*) and therefore further addition of KCl does not appear to influence the adsorption.

TABLE II

ADSORPTION OF MsTh-2 ON SINTERED GLASS IN THE PRESENCE OF KCl
(pH of the solution 9.5)

Concn. of KCl M	*MsTh-2 adsorbed c.p.m.*
0.00	6,619
0.02	6,969
0.5	6,800
0.10	6,647
0.20	6,728
0.50	6,791

The results shown in Table III clearly indicate that as the pH of the MsTh-2 solution increases, a correspondingly larger percentage of the activity settles at the bottom when the solutions are centrifuged; this is strong evidence for the formation of radiocolloid in MsTh-2 solutions.

TABLE III

CENTRIFUGATION STUDIES ON MsTh-2

pH	*Activity in the lower portion c.p.m.*	*Activity in the upper portion c.p.m.*	*% activity in lower portion*
1.5	5,630	8,450	40.0
2.5	5,180	8,780	37.1
4.0	7,900	6,462	55.2
6.0	9,160	4,110	69.0
7.5	11,021	1,203	90.1
9.0	13,331	1,072	92.5
9.8	12,569	1,071	92.1

The results obtained above clearly indicate that MsTh-2 in actinium behaves like a radiocolloid at pH 5. Further striking evidence for its behaviour as radiocolloid is obtained by paper chromatography. The distribution of Ba and the radioactivity due to MsTh-2 in the filter paper strip at different pH values are shown in Figs. 3–6. At pH 1.5 (Fig. 3), MsTh-2 moves with the solvent front and is detected only in the last zone; Ba also moves along with MsTh-2 since at this pH both of them are present in the ionic form. At pH 3 (Fig. 4), MsTh-2 moves only up to the second zone and at

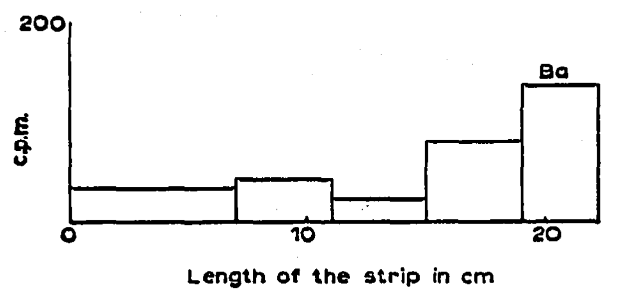

Fig. 3. Paper chromatogram of MsTh-2 and Ba at pH 1.5.

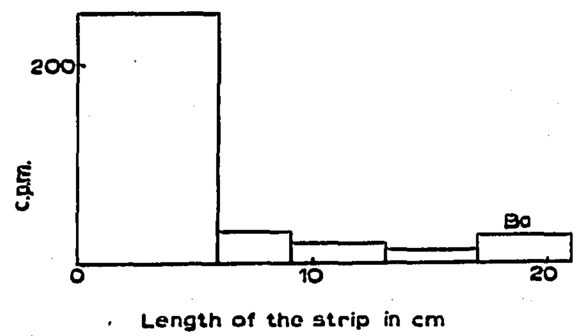

Fig. 4. Paper chromatogram of MsTh-2 and Ba at pH 3.0.

higher pH values it does not move out of the initial zone (Figs. 5 and 6). Ba moves along with the solvent front in all these cases and has been detected only in the last two zones, as shown in Figs. 3–6. The radiocolloid formation as indicated by these experiments seems to start at pH 3.0. This supports the observations made on the aged solutions of MsTh-2. Furthermore the paper chromatography strips appear to be better adsorbents than sintered glass.

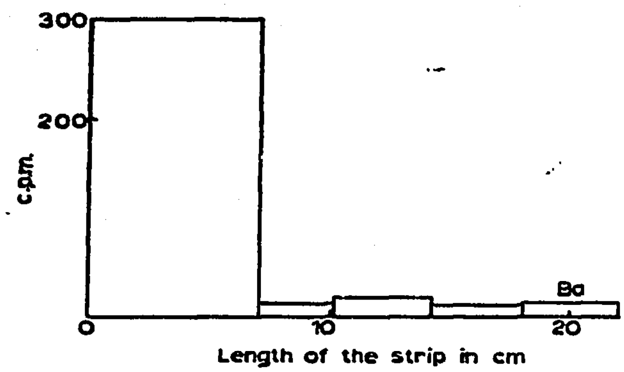

Fig. 5. Paper chromatogram of MsTh-2 and Ba at pH 8.0.

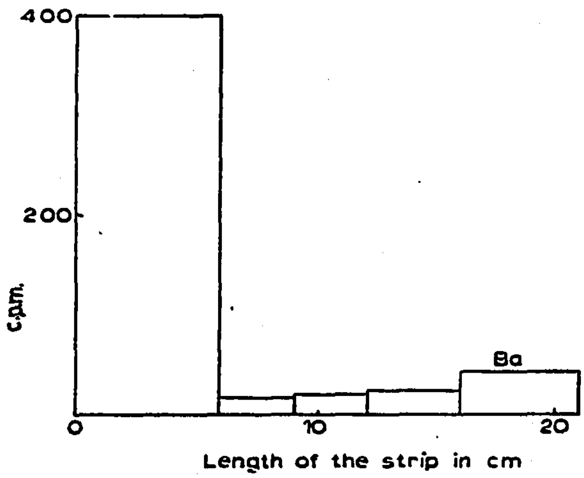

Fig. 6. Paper chromatogram of MsTh-2 and Ba at pH 9.5.

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SUMMARY

A report is given of the radiocolloidal behaviour of actinium as studied by adsorption on sintered glass and on paper.

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