SHORT COMMUNICATIONS

On the Anion-Exchange Behavior of Some Quadrivalent Actinide Elements

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It has been well established that thorium (IV) is not adsorbed on an anion exchange resin from hydrochloric acid solution of any concentration. This fact makes it possible to separate thorium(IV) cleanly from any elements which do form negative ions adsorbable on an anion resin[1]. In 1953, Jenkins and Richardson studied the uptake of thorium(IV) on an anion exchange resin such as Deacidite FF, from solutions containing nitrate and sulfate[2].

The present authors are continuing a systematic study on the adsorbability of quadrivalent actinide elements on anion-exchange resins. It has been observed that thorium(IV) is adsorbed on Dowex 1 both from sulfate and carbonate solutions, while neptunium(IV) is adsorbed from carbonate solutions. The good uptake of uranium(IV) on that resin from a sulfate solution was also observed.

Dowex 1-X8 of 100–200 mesh was employed in this experiment. In column studies, resin columns of 5.0 cm.×0.5 cm^2 were used. In equilibrium studies, Dowex 1 of sulfate form was first dried for three hours at 70°C and kept in a desiccator over a saturated solution of sodium bromide. The tracer solutions employed were thorium-234 in concentrated nitric acid and neptunium-239 in 6 N hydrochloric acid containing sulfur dioxide. The thorium(IV) solution was almost evaporated to dryness on a water bath and the residue was dissolved in solutions of ammonium sulfate or sodium carbonate of various concentrations. The neptunium (IV) solution was prepared by dissolving the residue in sodium carbonate solution containing a small amount of sulfur dioxide.

The radioactivity of the tracer was measured with a thin end-window Geiger-Müller tube after the tracer was coprecipitated with 5 mg. of ferric iron from acidified sample solutions with ferric hydroxide. In the case of samples containing thorium-234, the radioactive equilibrium between thorium-234 and protactinium-234 was attained at the time of measurement.

a) Experiments on thorium(IV) and uranium(IV) in solutions.

1) E. K. Hyde, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol, 7, 281 (1956).

2) I. L. Jenkins and R. J. Richardscn, A.E.R.E. C/R 1217. (1953).

i) Column studies.

After a resin bed of sulfate form was thoroughly washed with 0.1 M ammonium sulfate solution, 5 ml. of thorium(IV) solution was placed on the top of the column, and allowed to flow down through the column at a rate of 0.3–0.5 ml. per min.. The adsorption of thorium(IV) from 0.1 M ammonium sulfate solution was so complete that no activity of thorium-234 was detected in the effluent. The adsorbed thorium(IV) was easily eluted with 1 N hydrochloric acid solution. The elution curve is shown in Fig. 1.

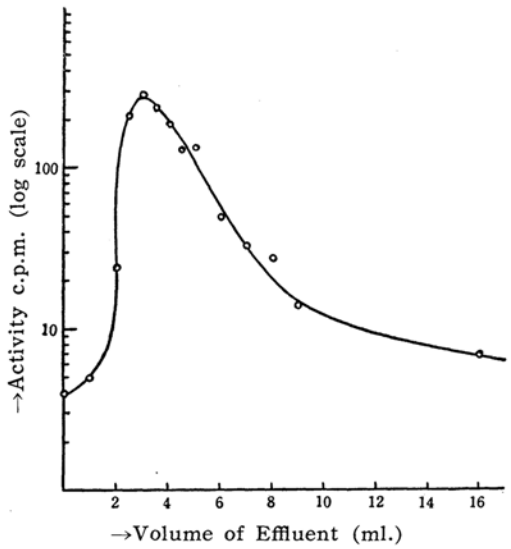

Fig. 1. The elution curve of Th(IV) with 1 N HCl. Column 5cm.×0.5cm² Dowex 1-X8 100-200 mesh.

Quadrivalent uranium, in macro quantities, was adsorbed on a resin bed of sulfate solution containing zinc, which was used for the reduction of uranyl ions. A green adsorption band appeared near the top of the bed. Washing of the column with 10 ml. of 0.01 M ammonium sulfate solution brought about no appreciable shift of the band. The adsorbed uranium (IV) was easily eluted with 6 N hydrochloric acid.

ii) Equilibrium studies.

Some experiments were carried out on thorium(IV). A weighed portion of the resin was allowed to stand overnight in a solution of ammonium sulfate under consideration. After the resin and the solution were placed in a glass-stoppered Erlenmeyer flask, the whole was shaken on a mechanical shaker in a thermostat at 25°C, until the exchange equilibrium was attained. In this case, a certain amount of thorium-232 was added to the tracer solution so that the equililbrium was reached at 0.1–1 % loading of thorium (IV) with respect to the resin capacity. The following values of the equilibrium distribution coefficient, K_d (activity per g. of resin/activity per ml. of solution) were obtained: at 25°C, K_d=21 for the adsorption of thorium(IV) from 1 M ammonium sulfate solution, K_d=310 from 0.01 M ammonium sulfate solution.

b) Experiments on thorium(IV) and neptunium(IV) in carbonate solutions.

Only column studies were carried out. Thorium(IV) was adsorbed on a resin bed from 0.1 M sodium carbonate solution. No activity of thorium-234 was detected in the effluent. A part of adsorbed thorium (IV) was eluted with 10 ml. of 4 M ammonium chloride. Then most part of thorium(IV) was removed with 20 ml. of 6 N hycrochloric acid solution. A similar adsorption of neptunium(IV) from 0.1 M sodium carbonate solution was observed in preliminary experiments. The nature of adsorption of these elements from carbonate solution is not clear as yet.

Details of the present study will be published elsewhere in the near future.

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