

THE DISTRIBUTION OF HEXAVALENT URANIUM AND  
TETRAVALENT THORIUM BETWEEN ALCOHOL-NITRIC ACID  
SOLUTIONS AND THE STRONGLY ACIDIC CATION EXCHANGER  
DOWEX-50

SEPARATION OF URANIUM FROM THORIUM

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One of the most characteristic phenomena observed in the course of our earlier studies on ion exchange in mixed solvents<sup>1-7</sup> is that the adsorption of uranium and thorium is much higher from mixed solvents than from pure aqueous acid solutions; furthermore it was found that the higher the alcohol percentage, the higher the distribution coefficient  $K_d$  of the adsorbed element. This has been explained by the decrease of the dielectric constant of the mixture, *i.e.* the decrease in the degree of dissociation of the salt, and its subsequent adsorption on the resin either as a neutral molecule or as a negatively charged complex<sup>5,6</sup>.

When carrying out the present work employing the cation exchange resin Dowex-50, we observed that the adsorption of both uranium and thorium is also much higher from mixed solvents than from pure aqueous acid solutions. Since we have found that both uranium and thorium are adsorbed as positively charged ions and not as complexes another type of mechanism must exist and some factors other than the dielectric constant of the mixture must be mainly responsible for the higher adsorption from mixed solvents than from pure aqueous acid solutions. On the other hand equilibrium studies have shown, that both hexavalent uranium and tetravalent thorium are strongly adsorbed on Dowex-50 from solutions containing a high alcohol percentage, whereas only thorium is strongly held from mixtures of low alcohol content, so that the two elements can be retained by the resin simultaneously from solutions of high alcohol content. Separation is achieved by eluting uranium with a mixture of 10% alcohol and 90% 1 *N* nitric acid, thorium being retained on the resin. Afterwards thorium can be removed by treating the resin with 3 *N* nitric acid.

EXPERIMENTAL

*Solutions and reagents*

The resin Dowex-50 (20-50 mesh, hydrogen form) was washed thoroughly with hot water to remove most of the organic impurities until the wash was colourless, then it was treated with approximately 200 ml of 6 *N* hydrochloric acid, and finally washed with cold distilled water to remove all acid. Afterwards the resin was washed with some methanol and dried at 50°.

The standard solutions of uranium and thorium contained the reagent grade nitrates dissolved in 1 *N* nitric acid (5 mg/ml).

The aliphatic alcohols, methanol, ethanol, *n*-propanol, and *n*-butanol were used.

#### *Quantitative determination of thorium and uranium*

The methods for the quantitative determination of thorium and uranium were exactly the same as those described in earlier papers<sup>3,4</sup>.

#### *Column operations; separation of uranium from thorium*

The column operations were carried out in columns of the same type and dimensions as those described earlier<sup>8</sup>.

Each column contained about 1.5 g of the dry resin. The columns were filled with the resin suspended in ethanol. The resin bed was then pretreated with 50 ml of a mixture consisting of 90 % ethanol and 10 % 1 *N* nitric acid. The sorption solution (45 ml ethanol + 5 ml 1 *N* nitric acid) containing thorium and uranium was passed through the column at a flow rate of about 20 ml/h. (Uranium was adsorbed in a zone of approximately 2 cm height.) The column was then washed with 200 ml of a mixture consisting of 10 % ethanol and 90 % 1 *N* nitric acid. During this step uranium is eluted. Uranium could be found to an extent of 60 % in the first 50 ml of the effluent, in the next 50 ml about 30 % of uranium could be detected, and the residual amount was found in a third 50 ml portion, while the last 50 ml portion was free from uranium. Afterwards the thorium was eluted with 3 *N* nitric acid. All the separation experiments in which micro- and milligram amounts of both uranium and thorium were employed were quantitative due to the fact that in 90 % ethanol the  $K_d$  values for uranium and thorium are 62,570 and 119,026, whereas in 10 % ethanol these values are 6 and 2,000 respectively. From Fig. 2 it is clear that the separation of uranium from thorium could also be accomplished in pure aqueous acid solutions at an acidity of 0.5 *N* nitric acid, but the simultaneous adsorption of both elements is hardly possible since the  $K_d$  for uranium in this case is only 31.

#### *Determination of distribution coefficients<sup>1-6</sup>*

The distribution coefficients  $K_d$  were always determined in a volume of 25 ml, employing 1 g of the resin and 5 mg thorium or uranium dissolved in 1 *N* nitric acid.

#### *Determination of exchange capacities*

The hydrogen capacity of the resin was found to be 4.1 mg equiv./g dry resin. The thorium and uranium capacities were determined by measuring the distribution coefficients<sup>5,6</sup> in 80 % methanol–20 % 1 *N* nitric acid mixtures at different concentrations of the elements. The volume was always 25 ml (20 ml methanol + 5 ml 1 *N* acid). We considered the maximum capacity of the resin to be that corresponding to the lowest  $K_d$ . A  $K_d$  of 20 for uranium was considered to be the one at which the resin is completely transformed to the uranium form; this low  $K_d$  compared with a  $K_d$  of 769,230 for a mixture of 5 mg uranium/25 ml was reached when the uranium concentration was 1 g/25 ml solution. The maximum capacity thus obtained was 450 mg uranium/g resin. On the other hand at a concentration of 400 mg thorium/25 ml the  $K_d$  is only 36.5, the amount taken up by the resin at this concentration being 235 mg thorium. By increasing the thorium content of the mixture to 500 mg thorium/25 ml ( $K_d = 22$ )

the amount retained by the resin remained practically constant, indicating that the resin was completely saturated with thorium.

#### General observation

When carrying out batch experiments it was noticed that the acidity of the alcohol-nitric acid mixtures increases after the adsorption of uranium, *i.e.* acid is formed. Furthermore uranium is not washed from the cation exchanger with water contrary to the case with anion exchangers. This indicates that both uranium and thorium are adsorbed as positive ions.

#### RESULTS

Fig. 1 shows the effect of the alcohol concentration on the  $K_d$ . The curves show, that the adsorption of both uranium and thorium increases with an increase in alcohol

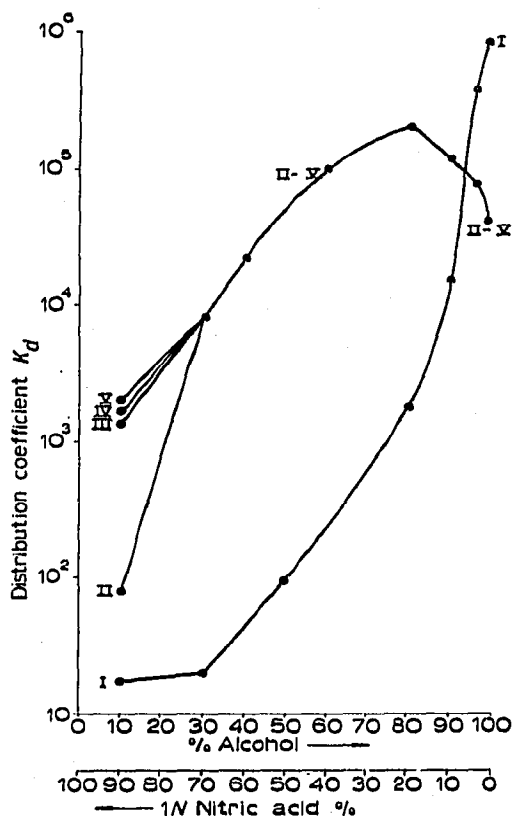


Fig. 1. Effect of alcohol concentration on the adsorption of uranium and thorium. I = uranium in methanol; II = thorium in *n*-butanol; III = thorium in *n*-propanol; IV = thorium in ethanol; V = thorium in methanol; II-V = thorium in methanol.

percentage, the maximum  $K_d$  for thorium being reached at 80 % alcohol ( $K_d = 200,000$ ). At higher alcohol percentages the value of  $K_d$  decreases (at 99 %  $K_d = 38,436$ ). In the case of uranium the distribution coefficient increases with an increase of the alcohol concentration; no peak is, however, noticed and the values of  $K_d$  cover a wider range (the  $K_d$  values for 10 % methanol and 99 % methanol are 17 and 769,230 respectively). Thorium also differs from uranium in that the value of  $K_d$  at all alcohol percentages above 30 % depends exclusively on the alcohol percentage rather than on the chain

length of the alcohols employed. That is the reason why in Fig. 1 in the range from 30 to 99 % only the results obtained in methanol, as a representative of all the other alcohols, have been recorded. At 10 % alcohol however, the chain length of the alcohol appears to play an important role, a continuous decrease of  $K_d$  occurring with increasing chain length of the alcohol (at 10 % the distribution coefficients for metha-

TABLE I  
EFFECT OF ALCOHOLS ON URANIUM ADSORPTION

Alcohol percentage	Ethanol	<i>n</i> -Propanol	<i>n</i> -Butanol
99	800,760	227,272	357,143
96	357,143	91,000	48,518
90	26,570	14,059	8,097
80	3,005	2,678	separation of 2 layers
60	520	243	separation of 2 layers
30	39	28	separation of 2 layers
10	8	11	23

nol and *n*-butanol are 2,000 and 81 respectively). In the case of uranium methanol cannot be taken as a representative for all alcohols because the distribution coefficient differs from one alcohol to another; because of this the  $K_d$  values for the other alcohols are given in a separate table (see Table I).

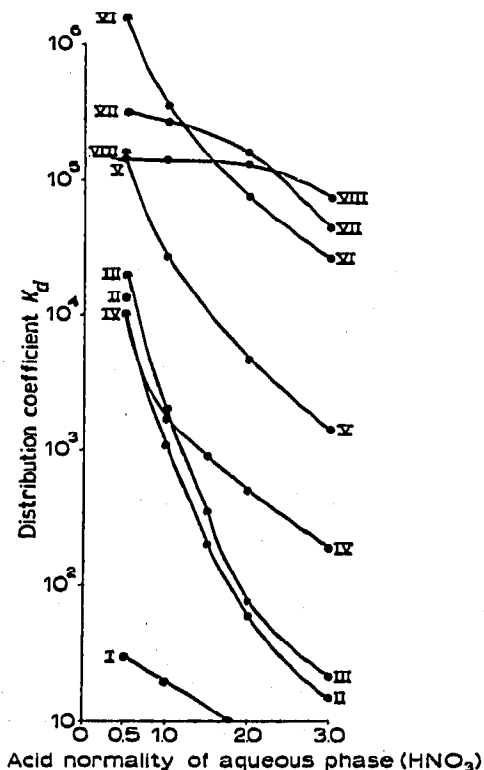


Fig. 2. Effect of nitric acid normality on the distribution coefficient of thorium and uranium in alcohol-nitric acid mixtures and in pure aqueous acid solutions. I = uranium in aqueous solution; II = thorium in aqueous solution; III = thorium in 10 % methanol; IV = uranium in 80 % methanol; V = uranium in 90 % methanol; VI = uranium in 96 % methanol; VII = thorium in 80 % methanol; VIII = thorium in 99 % methanol

At an alcohol content of 10% the chain length of the alcohol does not seem to have a similar effect as in the case of thorium. No results could be obtained for 80–30% *n*-butanol because of the formation of two separate layers.

Fig. 2 shows the effect of the nitric acid concentration, ranging from 0.5 *N* to 3 *N*, on the distribution coefficient of thorium and uranium in alcohol–nitric acid mixtures and in pure aqueous acid solutions.

From this figure it is clear, that the adsorption of both elements at all acid normalities is much higher from methanol–nitric acid mixtures than from pure aqueous acid

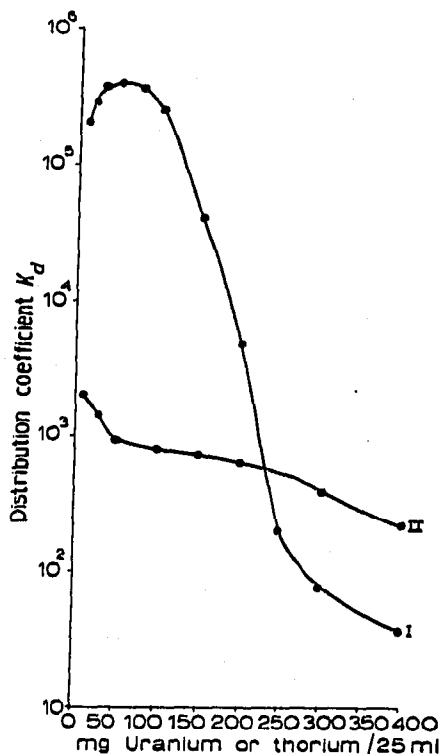


Fig. 3. Effect of the concentration of uranium or thorium on the distribution coefficient in 80% methanol–20% 1 *N* nitric acid. I = thorium; II = uranium.

solutions. It is also evident, that the distribution coefficient decreases with an increase of the acid normality. It has also been found that the extent of the adsorption is not only affected by the alcohol percentage and the acid normality but also by the presence of other ions. Thus in a mixture consisting of 96% methanol and 4% 1 *N* nitric acid (24 ml alcohol + 1 ml 1 *N* nitric acid) containing 5 mg uranium and 0.3 g ammonium nitrate, the  $K_d$  for uranium was found to be 222 compared with a  $K_d$  of 357,143 in the absence of ammonium nitrate. Fig. 3 shows the change of  $K_d$  (in 25 ml of mixtures containing 80% methanol and 20% 1 *N* nitric acid) at different concentrations of thorium and uranium. The values of  $K_d$  for thorium drop rapidly with increasing thorium concentration. For uranium the drop is much less for the same increase in the concentration of the element. This may be due to the difference in the ionic charge of the two elements.

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## SUMMARY

In the present work on ion exchange in mixed solvents a study was made of the adsorption behaviour of uranium and thorium on the strongly acidic cation exchange resin Dowex-50 in alcohol-nitric acid mixtures. Equilibrium studies have shown that both uranium and thorium are strongly adsorbed on this resin from solutions containing a high percentage of aliphatic alcohol. Based on these results some theoretical explanations of the adsorption behaviour of uranium and thorium could be given, and a method was developed for the quantitative separation of uranium and thorium by means of a column operation.

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