

THE ANION EXCHANGE BEHAVIOUR OF URANIUM AND THORIUM IN SULPHURIC ACID SOLUTIONS CONTAINING ALIPHATIC ALCOHOLS

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The distribution of uranyl ions between aqueous sulphuric acid solutions and strongly basic anion exchangers has been studied by KRAUS AND NELSON^{1,2} and other workers³, who found that uranyl is readily adsorbed from weakly acidic sulphuric acid solutions. This fact has been utilized for analytical purposes⁴⁻⁹. Thorium on the other hand is only adsorbed to a negligible extent from an aqueous sulphuric acid medium as shown by JENKINS AND RICHARDSON¹⁰, SAITO AND SEKINE¹¹ and KORKISCH AND FARAG¹². KORKISCH *et al.*¹³ and ANTAL *et al.*¹⁴ have investigated the adsorption behaviour of uranium and thorium in ethanol-mineral acid mixtures including sulphuric acid solutions. It was observed that the adsorption of these actinide elements from sulphuric acid solutions is strongly enhanced by the introduction of ethanol. This work has now been completed and extended to other aliphatic alcohols. The experimental results presented show that extremely high distribution coefficients for uranium and rather high distribution coefficients for thorium are reached in alcohol-sulphuric acid mixtures of high alcohol percentage. The adsorption of uranium and thorium on Dowex 1 (sulphate form) was found to increase with increasing alcohol content and decreasing over-all acidity of the mixtures. No effect of chain length and dielectric constant of the alcohols could be observed, whereas a marked influence of the dielectric constant and chain length of alcohols has been found in hydrochloric¹⁵ and nitric acid¹⁶-alcohol systems.

EXPERIMENTAL

Reagents and solutions

Resin. Dowex 1 X8, (100-200 mesh, sulphate form, air dried).

Alcohols. The aliphatic alcohols, methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and isobutanol, reagent grade solvents, were used.

Uranium and thorium solutions. Exactly weighed amounts of uranium nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and thorium nitrate ($\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$) were dissolved in 5 *N* nitric acid and the content of these solutions was standardized gravimetrically¹⁷ (uranium) or spectrophotometrically¹⁸ (thorium). Standard uranium and thorium sulphate solutions were prepared directly from aliquots of these stock solutions by twice cautiously fuming off with concentrated sulphuric acid and taking up the residue in sulphuric acid of suitable normality. Uranium standard solutions containing 1, 10, and 100 mg uranium/ml and standard thorium solutions containing 1 mg and 200 μg thorium/ml were prepared.

Apparatus

All spectrophotometric measurements were carried out with a Beckman model B spectrophotometer using 1 cm cells, while the polarographic determination of uranium was performed by means of a Metrohm Polarecord type E, 261 R polarograph. For the fluorimetric measurements of uranium a Galvanek Morrison, Mark V, fluorimeter was utilized.

Determination of uranium

After separation of the resin uranium was determined in the filtrates polarographically or, in cases where very small amounts were present, fluorimetrically. To this end the filtrates were evaporated and the sulphuric acid carefully fumed off in a quartz dish. The residues were ignited and evaporated twice with 6 N hydrochloric acid on the steam bath. The residues were then taken up in 0.01 N nitric acid for polarographic measurements^{19, 20}. When very small amounts of uranium had to be assayed the fluorimetric method described by SCHÖNFELD *et al.*²¹ was employed.

Determination of thorium

Thorium was determined spectrophotometrically using Thoronol¹⁸ or Solochrome Fast Red^{22, 23}. The filtrates were processed in the following way: After evaporation and fuming off of the sulphuric acid in a platinum dish the residues were ignited for a short time and a few milliliters of a 1 + 1 mixture (v/v) of concentrated hydrofluoric and nitric acids were added. As soon as the dish was dry the residue was treated 5 times successively with a few milliliters of nitric acid each time evaporating to dryness on the steam bath. The residue was dissolved in a few milliliters of 0.1 N hydrochloric acid if the Thoronol method¹⁸ was employed, or in 1 ml 1 N hydrochloric acid if Solochrome Fast Red was used as the spectrophotometric reagent, after which the procedure was the same as that described elsewhere^{22, 23}. For the destruction of organic matter an alternative method using perhydrol may be applied²⁴.

Determination of distribution coefficients and exchange capacity

The distribution coefficients ($K_d = \mu\text{g}$ uranium or thorium per g resin divided by μg uranium or thorium per ml solution) were determined by a batch equilibrium method in volumes of 25 or 50 ml of the various sulphuric acid-alcohol mixtures containing varying amounts of thorium or uranium and 1 g resin for each experiment. The maximum uranium capacity was determined for a mixture containing 90 % *n*-propanol and 10 % 1 N sulphuric acid and was found to be 210 mg uranium/g dry resin (sulphate form). This capacity was found when 220 mg of uranium or more were present in the solution. Since the sulphate capacity of the resin was known (3.4 mg equiv./g dry resin) a stoichiometric formula for the uranyl sulphate complex on the resin could be calculated (see pp. 513, 514). No maximal exchange capacity for thorium was determined since the solubility of thorium sulphate in mixtures of sulphuric acid and alcohols is relatively small ($2.3 \cdot 10^{-5}$ moles of thorium are soluble in 1 l mixture containing 90 % methanol + 10 % 2 N sulphuric acid).

RESULTS

From Fig. 1 it can be seen that the distribution coefficients of uranium and thorium in sulphuric acid-alcohol mixtures increase with the alcohol percentage in the solutions.

Curves I and II are valid for all the aliphatic alcohols investigated since there is no variation of the distribution coefficient if an alcohol in any given mixture is replaced by any other alcohol. With the butanols, however, two liquid layers were formed up to a content of 90 % of these alcohols in the solution, wherefore distribution coefficients

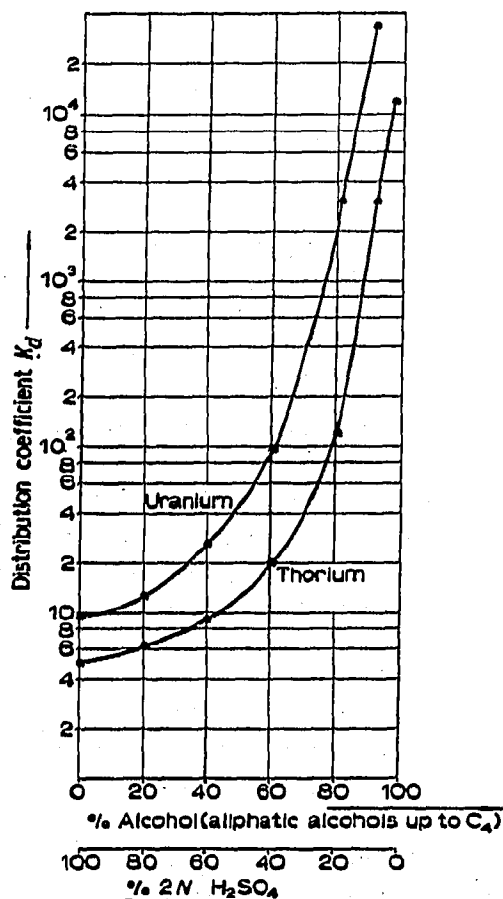


Fig. 1. Effect of concentration on the adsorption of uranium and thorium on Dowex I from sulphuric acid-alcohol mixtures.

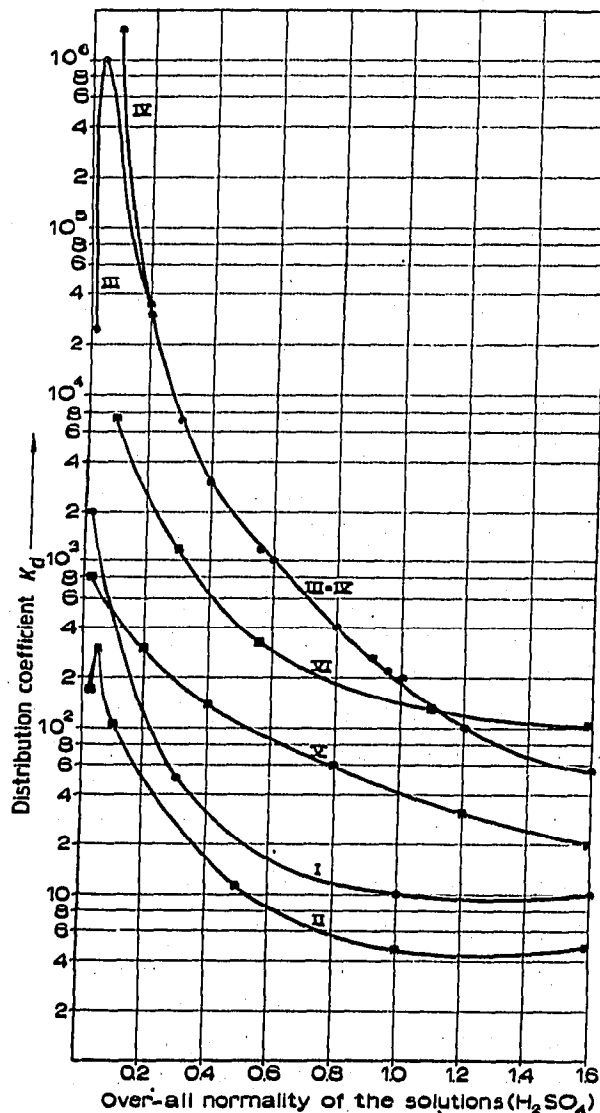


Fig. 2. Effect of sulphuric acid normality on the adsorption of uranium and thorium. I = uranium in 100 % H_2SO_4 (KRAUS AND NELSON); II = thorium in 100 % H_2SO_4 ; III = uranium in 80 % alcohol; IV = uranium in 90 % alcohol; V = thorium in 80 % alcohol; VI = thorium in 90 % alcohol.

were only determined in solutions of high alcohol percentages (90 and 96 %) where only one phase existed.

Fig. 2 illustrates the effect of the over-all acidity on the distribution coefficient in solutions of constant alcohol content. There is a steep rise at low sulphuric acid

normalities so that differences from one up to three orders of magnitude exist between the distribution coefficients of uranium (thorium) in the alcohol mixtures and in aqueous solutions of corresponding sulphuric acid normalities (compare curves I and II with curves III, IV, V and VI).

To show the influence of concentration on the adsorption of uranium a K_d -versus concentration curve is presented in Fig. 3, from which it is evident that the distribution coefficient of uranium decreases rapidly with increasing uranium con-

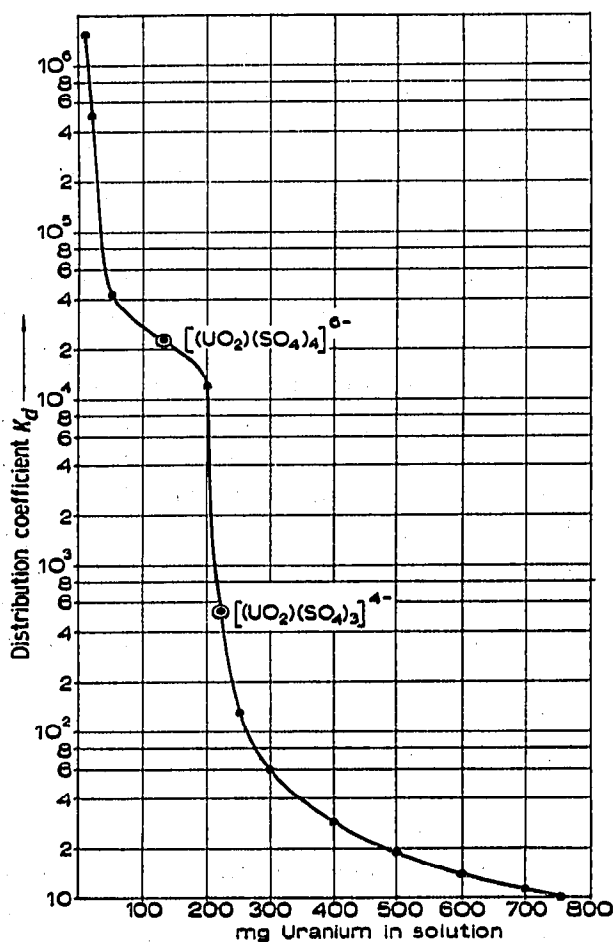


Fig. 3. Effect of concentration of uranium on the distribution coefficient in 90% alcohol-10% H_2SO_4 .

centration in a solution containing 90% alcohol + 10% 1 N sulphuric acid. The same can be expected for thorium under identical conditions. Because of the rather low solubility of thorium sulphate in sulphuric acid-alcohol mixtures (see p. 511) it seemed, however, of no practical value to investigate the effect of thorium concentration on the K_d in such systems. From the maximum amount of uranium adsorbed on 1 g dry resin (exchange capacity = 210 mg uranium) and the sulphate capacity the number of charges of the complex on the (saturated) resin was calculated using the simple relationship

$$n = \frac{C_r \times A}{C_e}$$

where n = number of negative charges, C_r = sulphate capacity (3.4 mg equiv./g dry resin), A = atomic weight of uranium and C_e = exchange capacity in mg. Since n was found to be 3.85, a value of 4 negative charges seemed to be relevant which applies to the trisulphato complex $[(\text{UO}_2)(\text{SO}_4)_3]^{4-}$. For the encircled point in the middle of the first (smaller) step of the curve n can—if the amount of uranium taken up by the resin at that point (practically 135 mg) is substituted for C_e in the above equation—be calculated $\cong 6$, which corresponds to a tetrasulphato complex $[(\text{UO}_2)(\text{SO}_4)_4]^{6-}$.

DISCUSSION

Although it is generally known that the introduction of alcohols into ion-exchange systems can greatly increase the adsorbability of many ions, the extraordinarily high distribution coefficients which were found for uranium in sulphuric acid–alcohol mixtures of high alcohol content are somewhat surprising. An explanation can be found in the mechanism of uranium adsorption on anion exchangers from aqueous sulphuric acid medium. According to the investigations of ARDEN AND WOOD²⁵ and others^{15, 26} neutral adsorption accounts for the adsorption of uranium (thorium) from dilute sulphuric acid solutions on strong base anion exchangers. The extremely high distribution coefficients in mixtures of high alcohol content can thus be readily explained by the fact that neutral adsorption increases with increasing alcohol concentration as has been observed previously²⁷. The two-stepped curve in Fig. 3 indicates that two uranyl sulphato complexes are formed on the resin. Starting with small concentrations the tetrasulphato complex (see above) will be formed until the resin is saturated (encircled point on the first step). Further adsorption becomes possible with increasing concentration as the tetrasulphato complex is gradually transformed into the trisulphato complex (see above). As soon as stoichiometry is attained no more adsorption can take place. Since the existence of the uranyl tri- and tetrasulphato complexes has also been proved by ARDEN AND WOOD²⁵ in aqueous sulphuric acid anion-exchange systems, we may take it that the same mechanism of adsorption is effective in aqueous and in alcohol–sulphuric acid mixtures, *i.e.* neutral adsorption.

APPLICABILITY

From the results obtained the possibility for simultaneous adsorption of high amounts of uranium and small amounts of thorium (because of low solubility) from a mixture containing 90 % alcohol + 10 % dilute sulphuric acid is obvious, while a separation of these two radioelements can be carried out with 80 % alcohol in the mixtures.

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SUMMARY

The anion exchange behaviour of uranium and thorium in sulphuric acid–alcohol media was investigated employing the strongly basic anion exchanger Dowex 1 X8. Extremely high distribution coefficients for uranium were found, for which a theoretical explanation is offered.

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