wird mit einem geeigneten Detektor besprüht und die Schicht im Tageslicht und im U.V.-Licht inspiziert.

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Notes

The distribution of hexavalent uranium between alcohol–nitric acid solutions and the strongly basic anion exchanger Dowex-1

In continuation of the work of KORKISCH *et al.*[1] and TERA *et al.*[2] on the distribution of uranium and thorium between alcohol–mineral acid solutions and the strongly basic anion exchanger Dowex-1, we have investigated the adsorption of uranium from nitric acid solutions containing aliphatic alcohols, *viz.* methanol, ethanol, etc. In an earlier paper[3] on the distribution of uranium between hydrochloric acid–alcohol solutions and the same resin, facts leading to the explanation of the very probable adsorption mechanism of uranium[3] were put forward, and these facts are also applied here to explain the adsorption mechanism of uranyl ions under the experimental conditions employed in the present investigation.

Experimental

Solutions, reagents and quantitative determination of uranium. Air-dried Dowex-1, X8 (100–200 mesh, nitrate form) was used. The aliphatic alcohols (methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, and a mixture of the amyl alcohols) were reagent grade solvents. The standard solution of uranium contained the reagent grade nitrate $(UO_2)(NO_3)_2 \cdot 6H_2O$ dissolved in 5 N nitric acid.

Uranium determinations in the filtrates after removing the resin were carried out polarographically as described earlier[1–3].

Determination of distribution coefficients and exchange capacities. The distribution coefficients K_d[4] were determined in volumes of 25 and 50 ml of the mixture. For each experiment 5 mg of uranium and 1 g of resin were used, and the equilibrium experiments were carried out as described earlier[1–4]. The results shown in Figs. 1–3 were obtained using this procedure.

The nitrate capacity of the resin was found to be 4.4 mg equiv./g dry resin. The maximum uranium capacity was determined by batch experiments in 98 % *n*-propanol–2 % 5 *N* nitric acid mixtures using different uranium concentrations. This capacity was reached when the uranium concentration was 400 mg uranium/50 ml mixture, and had a value of 212.5 mg/g dry resin, which was found to be practically constant at higher uranium concentrations and corresponded to a K_d of 56.

Results

Fig. 1 shows the effect of the alcohol concentration on the distribution coefficient K_d. The curves show that the adsorption of the uranium nitrate complex on the resin is highest in an amyl alcohol medium, and lowest in methanol medium. This effect is reversed when thorium is used instead of uranium[2].

From Fig. 1 it is also clear that the adsorption of uranium at higher percentages of alcohol increases with increasing chain length of the alcohols employed. At lower alcohol concentrations this regularity is disturbed, possibly due to partial ester formation. The K_d obtained in isopropanol and isobutanol mixtures are not shown in Fig. 1 since they were found to be virtually identical with those of the corre-

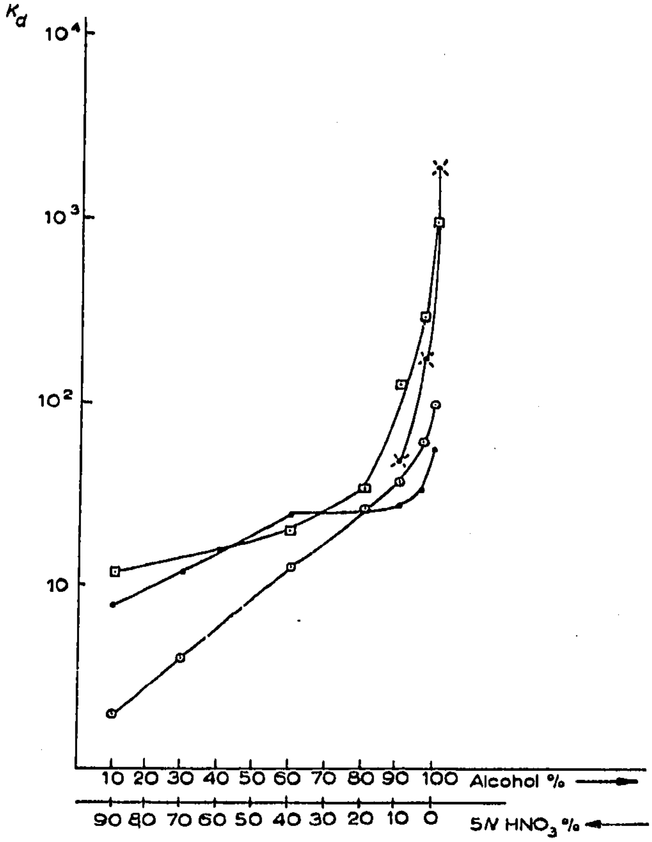


Fig. 1. Effect of the alcohol concentration on the distribution coefficient K_d. ●—● methanol; ⊙—⊙ ethanol; ⊡—⊡ *n*-propanol; ×—× amyl alcohol.

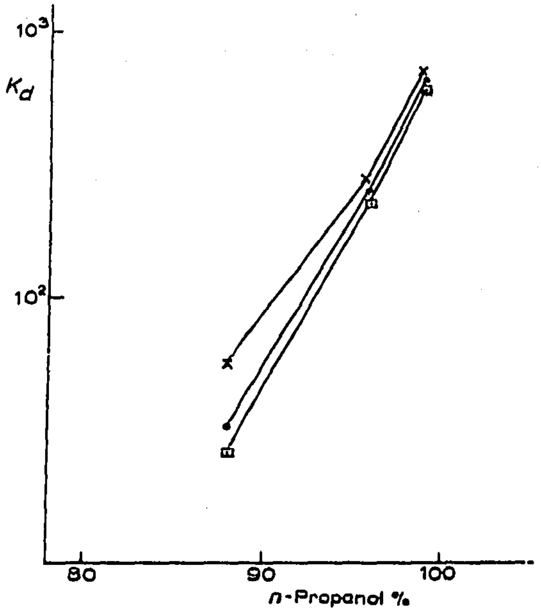


Fig. 2. Relationship between the distribution coefficient K_d and the acid concentration in n-propanol–nitric acid media. ⊡—⊡ 1 N HNO_3; ●—● 3 N HNO_3; ×—× 5 N HNO_3.

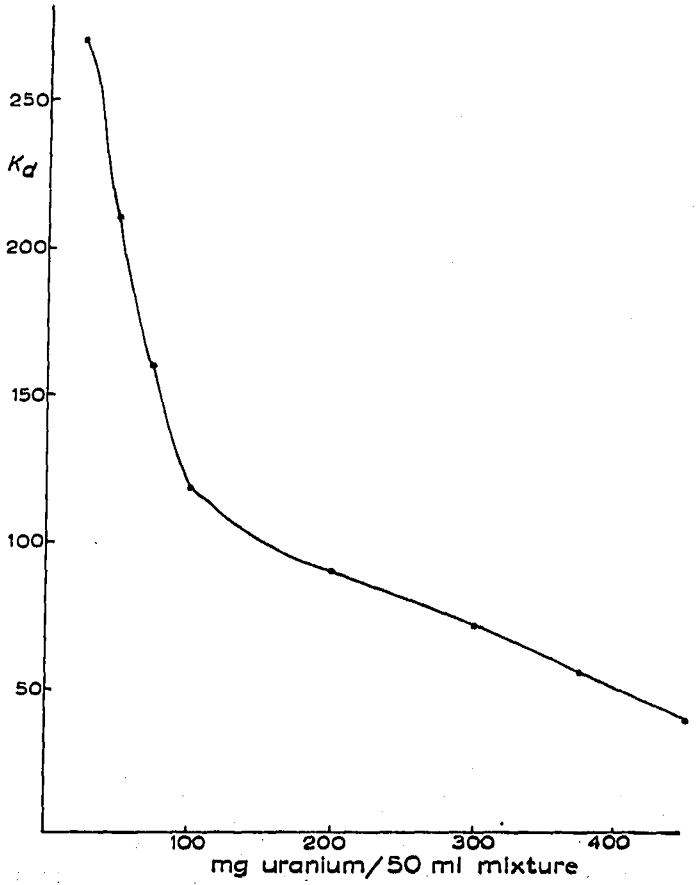


Fig. 3. Relation between K_d and uranium concentration.

sponding *n*-alcohols. The general increase of the distribution coefficient with increasing alcohol percentage and growing chain length of the alcohols appears to be due to those facts that have been discussed in detail elsewhere[3]. Other factors governing the extent of adsorption may be the degree and type of solvation as well as esterification.

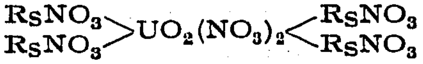
In Fig. 2 the relationship between the distribution coefficient K_d and the acid concentration in *n*-propanol–nitric acid media is shown. From this figure it can be seen that in the range from 1–5 N nitric acid the adsorption increases with increasing normality of the acid. This increase, however, is much more pronounced at lower alcohol percentages.

Fig. 3 shows the change in K_d with increasing uranium concentration. The rapid decrease of the distribution coefficient with increasing content of uranium of the mixture suggests the presence of only one form of uranium nitrate complex[3].

Discussion

The mechanism of uranium adsorption can be explained in the same manner as has earlier been described for the adsorption of the negatively charged chloride complex of uranium[4]. The experimental results obtained in the determination of the exchange capacities for nitrate and uranium (see experimental part) suggest that a complex of the following formula exists in the resin: $(UO_2(NO_3)_6)^{4-}$. Based on this assumption the theoretical capacity should be $\frac{3.4 \times 238}{4} = 202.3$ mg uranium/g dry resin.

Since the experimental value of 212.5 mg obtained is in rather good agreement with the theoretical value given above, it is very likely that uranium is adsorbed on the resin as:



$$\begin{matrix}RsNO_3\\RsNO_3\end{matrix}\!>UO_2(NO_3)_2<\!\begin{matrix}RsNO_3\\RsNO_3\end{matrix}$$

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