

SORPTION BEHAVIOUR OF SOME ACTINIDES ON SILICA GEL FROM MINERAL ACIDS AND ALCOHOLIC SOLUTIONS

N. SOUKA, K. FARAH, R. SHABANA

*Nuclear Chemistry Department, Atomic Energy Establishment,
Caïor (Egypt)*

(Received March 8, 1976)

Sorption of Th, Pa, U, Np and Pu on silica gel from HNO₃, HCl and HCl – ROH solutions was investigated. Equilibrium studies indicated sorption behaviour to vary greatly with the acid used. In mixtures of HCl with different alcohols, distribution coefficients were found to depend on alcohol percentage as well as on acidity. Results were discussed and conditions for possible separations were indicated.

Introduction

The use of silica gel in the separation of radio-elements has received increasing interest.¹⁻⁴ Mutual separations between zirconium, niobium, uranium and plutonium have been experimented with this exchanger.⁵ The ion-exchange properties of this material have been investigated by many authors.^{1,2,4,6}

The present work is an investigation of the sorption behaviour of thorium, protactinium, uranium, neptunium and plutonium on silica gel from HNO₃, HCl and HCl – alcohol mixtures. The main object of the study is to investigate how alcohols will affect the sorption of the mentioned elements.

Experimental

Chemical reagents used in the present investigation were of analytical grade. ²³⁴Th, ²³³Pa, ²³³U, ²³⁹Np and ²³⁹Pu were used for tracing thorium(IV), protactinium(V), uranium(VI), neptunium(V) and plutonium(IV) and were assayed radiometrically according to their specific radiations.

Chromatographic silica gel, a product of BDH was used as sorbent and was heated before use for 2 hours at 120 °C. Exact thermal treatment was followed for all batches.

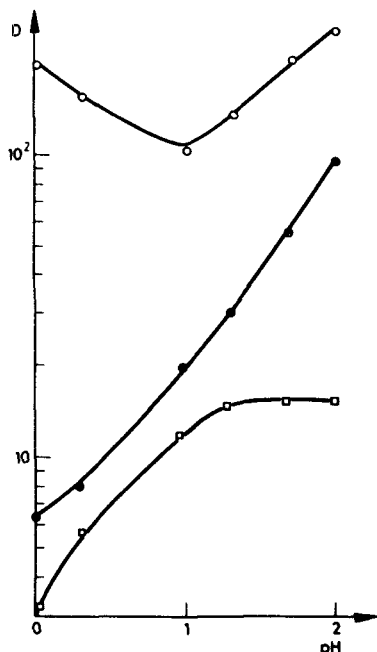


Fig. 1. Effect of pH on sorption of Th, Pa and Np on silica gel: ● – Th; ○ – Pa; □ – Np

Sorption studies were carried out under static conditions by batch equilibration at room temperature. Distribution studies indicated equilibrium to be attained in about three hours. Each D value ($\text{g} \cdot \text{ml}^{-1}$) is an average of three separate determinations.

Results and discussion

Effect of pH on sorption

The effect of pH on the sorption of Th, Pa and Np is given in Fig. 1. It is clear that the distribution of Th and Np increases of pH. D_{Pa} on the other hand decreases, passing by a minimum round $\text{pH} = 1$ and then increases. In the investigated range of pH, silica gel was reported to behave as a cation exchanger.⁶ The sorption behaviour of Th and Np resembles very much that expected in cation exchange equilibria. Results obtained on protactinium sorption are in close agreement with those found by SPITSYN et al.⁴ These authors indicated the kinetics of Pa sorption by silica gel to be of an internal diffusion nature and the rate of establishment of equilibrium to depend on $[\text{H}^+]$, passing by a minimum in the region 0.5 – 1.5M.

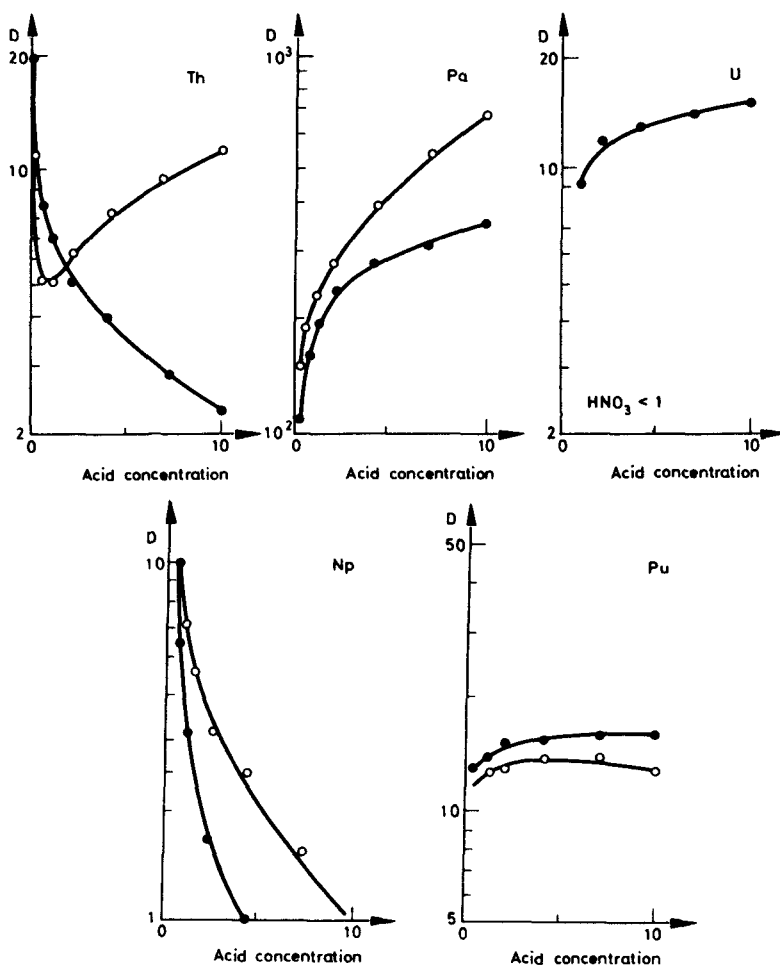


Fig. 2. Effect of acid concentration on sorption of Th, Pa, U, Np and Pu on silica gel: \circ – HNO₃; \bullet – HCl

Plutonium distribution coefficients at $\text{pH} > 0$ were not entirely reproducible probably due to the presence of polynuclear aggregates as well as possible disproportionation. Distribution coefficients of uranium in the working solutions indicated values < 1 .

Effect of acid concentration on sorption

The sorption behaviour of Th, Pa, U, Np and Pu on silica gel from HCl and HNO₃ solutions is given in Fig. 2. It is clear that the distribution coefficients of

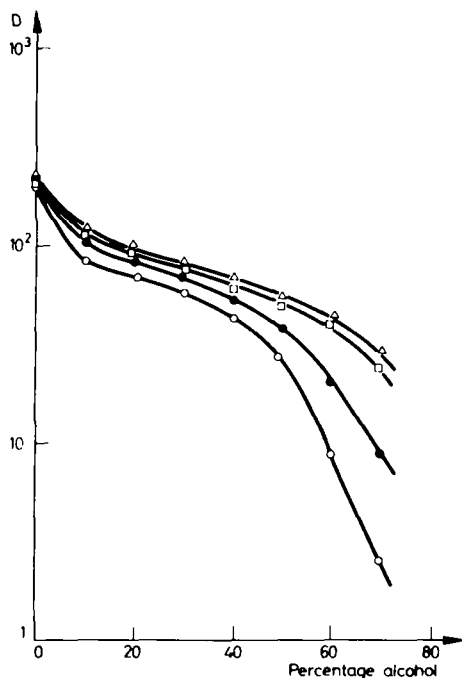


Fig. 3. Effect of different alcohols on sorption of Pa on silica gel: Δ – Methanol; \square – Ethanol; \bullet – n-Propanol; \circ – Isopropanol

the mentioned elements change from one medium to another and depend on acid concentration.

Data given in Fig. 2 indicate, an increase in D_{Pa} and a decrease in both D_{Th} and D_{Np} with increase of $[HCl]$. The sorption of uranium and plutonium on the other hand seems to be slightly affected by increase of acid concentration. The sorption behaviour of Pa, Np and Pu from HNO_3 solutions acquires more or less the same general behaviour as that from HCl solutions. On the other hand, D_{Th} decreases with HNO_3 concentration, up to 1M and then increases.

Studies on the ion exchange character of silica gel indicated that at $[H^+] > 1M$ it may behave as an anion exchanger.⁶ The observed decrease in D_{Th} and D_{Np} with increase of HCl concentration, may be explained by the absence of anionic chlorocomplexes of these metal ions, while the increase in D_{Th} in HNO_3 solutions may be related to the sorption of its anionic nitrate complexes. In the investigated solutions, Pa was reported to exist in a series of cationic, neutral and anionic species of the general form $PaO_x(OH)_yA_z^{5-2x-y-z}$,^{7,8} where $x = 0$ to 2, $y = 0$ to 4,

and $z = 0$ to 8 and $x + y + z \leq 8$. SPITSYN et al.⁴ indicated Pa sorption on silica gel at moderate and high acidities to be mainly due to the uptake of neutral species of the type $\text{Pa}(\text{OH})_n\text{Cl}_{5-n}$.

Effect of alcohols on sorption

The effect of increasing amounts of methanol, ethanol, n-propanol and isopropanol on D_{Pa} at a constant HCl concentration of 3.5M HCl is given in Fig. 3. A decrease in D-values with increase of alcohol percentage has been noticed. For the same alcohol and acid concentrations D-values take the sequence: isopropanol < n-propanol < ethanol < methanol. This sequence seems to be parallel with that of increasing 1/D.C. of the medium, and is more pronounced at high alcohol concentrations than at lower ones.

It has been indicated by KORKISCH et al.,⁹ that the addition of alcohols to ion exchange equilibria modify the properties of both aqueous and resinous phases. In the present work discussions will be limited to changes taking place in the aqueous phase, since information about swelling and solvent uptake in the investigated equilibria is not available.

A systematic investigation on the effect of increasing amounts of isopropanol on D_{Pa} at different HCl concentrations is given in Fig. 4. It can be deduced that at acidities > 3M, D_{Pa} decreases continuously with increase of alcohol concentration. At lower acidities sorption first decreases passing by a certain flattened minimum and then increases. As mentioned before protactinium exists in solution in a series of cationic, neutral and anionic species and it is sorbed on silica gel as both cationic and neutral species depending on acidity. The addition of alcohols leads to a progressive increase of ionic interactions favouring the formation of highly charged anionic complexes. This explains the observed decrease in D_{Pa} with the increase of alcohol at acidities above 3M. The decrease in D_{Pa} by addition of alcohol at HCl concentrations 1 and 1.5M may be attributed to the gradual transformation of hydroxy Pa species to less sorbed forms. The increase in sorption at higher alcohol concentrations may be attributed once more to the formation and selective sorption of neutral Pa species.

The effect of increasing percentages of isopropanol on sorption of NpO_2^+ at different HCl concentrations of 0.2, 0.5, 0.7 and 1M is given in Fig. 5. It is clear that D_{Np} increases with increase of alcohol concentration. At $[\text{H}^+] < 1\text{M}$, silica gel is expected to behave as a cation exchanger and the increase in D_{Np} may be explained by the dehydrating action of alcohols.⁹ Decrease of D.C. of the medium is known to affect the hydration of hydrated ions leading to more favourable sorption conditions.

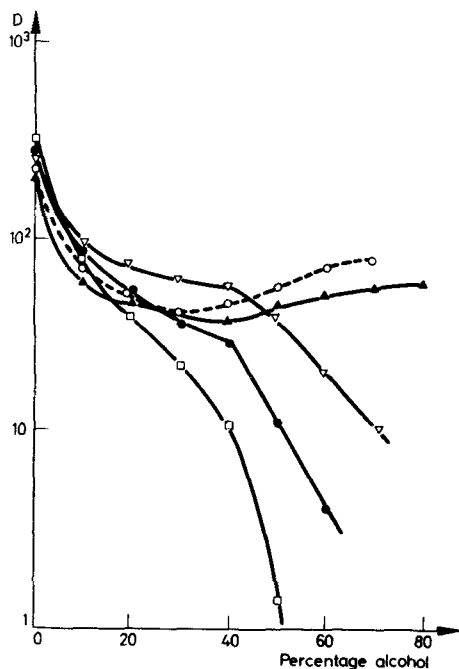


Fig. 4. Effect of isopropanol concentration on sorption of Pa on silica gel from HCl solutions: □ - 6M; ● - 4.5M; ▽ - 3M; ▲ - 1.5M; ○ - 1M

The data given in Fig. 2 indicate that at moderate [HCl], Th, U and Pu have low uptakes on silica gel. An investigation of the effect of alcohols on the sorption of these elements indicated practically no variations in distribution coefficients (Table 1).

From the fore-cited data, it is clear that alcohols affect differently the sorption behaviour of actinide elements on silica gel. Sorption coefficients were found to depend greatly on acid and alcohol concentrations.

Possible separations

Data given in Fig. 2 indicate that with the exception of Pa, the studied actinides have all negligible sorption coefficients. In general, the addition of alcohols decreases D_{Pa} , the decrease is more pronounced at high HCl concentrations. These results can be applied to the isolation of ^{233}Pa from irradiated thorium.

Best separation of the two elements can be achieved when loading the silica column from a 10M HCl solution. Thorium percolates while Pa is retained. After

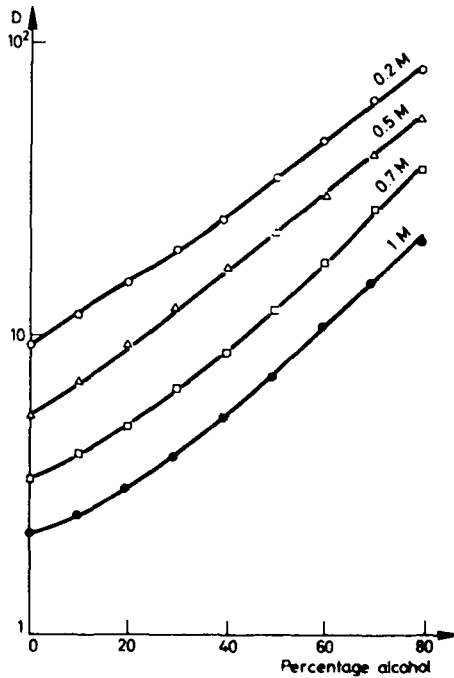


Fig. 5. Effect of isopropanol concentration on sorption of Np on silica gel from HCl solutions

washing the column with several column volumes of 10M HCl, protactinium can be eluted quantitatively with a mixture of 50% 12M HCl + 50% isopropanol.

The suggested method can be extended to the separation of ^{231}Pa from irradiated thorium provided special leaching is undertaken. The isolated ^{231}Pa can be used for production of ^{232}U .

Table 1
Effect of isopropanol concentration on sorption of Th(IV), U(VI) and Pu(IV) on silica gel from 1.5M HCl

Isopropanol, %	D_{Th}	D_{U}	D_{Pu}
0	7.2	9.6	15.5
20	4.8	5.8	13.7
40	3.2	8.8	7.3
60	5.3	15.0	11.0
80	8.2	20.0	17.0

References

1. S. AHRLAND, I. GRENTHE, B. NOREN, Acta Chem. Scand., 14 (1960) 1059.
2. E. AKALSU, R. ONO, K. TSUKUECHI, H. UCHIYAMA, J. Nucl. Sci. Technol., 2 (1965) 141.
3. M. ZAKI, I. MONEIM, Z. Anorg. Allg. Chem., 360 (1968) 208.
4. V. SPITSYN, R. DYACHKOVA, A. KAMONKAYER, Sov. Radiochem. (Eng. Transl.), 14 (1972) 230.
5. C. LOWE, M. MCEWEEN, F. MEAD, AECD-4066, 1950.
6. S. AHRLAND, R. ONO, K. TSUKUECHI, H. UCHIYAMA, J. Nucl. Sci. Technol., 14 (1965) 1077.
7. R. GUILLAUMONT, Rev. Chim. Miner., 3 (1966) 339.
8. R. GUILLAUMONT, C. MIRANDA, Rev. Chim. Miner., 3 (1966) 861.
9. J. KORKISCH, G. JANAUER, Talanta, 9 (1962) 957.