STUDY ON CHEMICAL SPECIATION OF THORIUM IN MICROCONCENTRATION AQUEOUS SOLUTION IN THE PRESENCE OF INORGANIC LIGANDS

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abstract: Total stability constants of complex species formed by Th^{4+} ions with F^- and $H_2PO_4^-$ ions where determined in microconcentration aqueous solutions. A method based on experimental determination of the global repartition coefficients of $^{234}Th^{4+}$ radionuclide between aqueous phases and a benzene solution of tributylphosphate (20% v/v) was applied. These global coefficients were determined either in the presence or the absence of anionic ligands in the aqueous solution at various concentrations. The stability constants were used to establish the chemical speciation, or the concentration for all the chemical forms existing in the studied system in correlation with aqueous phase concentration of ligands.

Introduction

Large quantities of low activity water become liquid wastes in nuclear technologies and, especially, in nuclear fuel manufacture or chemical reprocessing of burned fuels from the nuclear power plants. These residual waters may contain quantities, some time at appreciable level, of uranium and thorium as well as large series of anionic species that would form either ionic or neutral complex species with Th^{4+} or UO_2^{2+} ions. The efficient decontamination of these residual waters can be made before spreading in the environment, due to the proper information on the **chemical speciation** of each radionuclide that is contained. One of the methods used for this attending purpose is the study on the radionuclide distribution between an aqueous phase, which contains ligands in various concentrations, and an organic phase, immiscible with water, which contains a reagent that allows the radionuclide transfer into this phase [1÷4]. The global stability constants of complex species formed by the radionuclide with the ligand, can be determined starting from the dependence of the global distribution coefficients between the two phases, aqueous and organic, and the ligand concentration in aqueous phase [5,6]. The chemical speciation of the radionuclide in the aqueous solution can be calculated using overall stability constants [7,8].

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Experimental

In experimental works we used $^{234}_{90}\text{Th}$ radionuclide, often named UX_1. It is generated directly by α–decay of $^{238}_{92}\text{U}$ radionuclide, from, its half-life being 24.1 days. Consequently, it is present in micro concentration in all uranium salts older then 5-6 months. Knowing that half-life of $^{238}_{92}\text{U}$ is $4.5\cdot10^9$ years, it can be calculated the amount of hexa hydrate uranyl nitrate which contains, at equilibrium, a certain UX_1 quantity (in activity units):

$$m_{\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}}\ (g) = 6.32\cdot\Lambda_{UX_1}\ (\mu\text{CI}) \qquad (1)$$

For approximately 10 μCi UX_1 are, therefore, necessary 63.2 g of $\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}$.

UX_1 radionuclide was separated using ionic exchange. For this purpose, approximately 30 g of 50-100 mash Dovex-50×8, cation exchanger in H^+ form, were maintained 5 hours in distilled water to establish the swollen equilibrium. Then, a chromatographic column, 12 mm in diameter and 50 cm height, was filled with this resin. The column was washed firstly with 250 mL of distillate water and then with 0.5 mole·L^{-1} HCl solution. Finally, the column was washed with distilled water until the Cl^- anions were absent in the effluent (negative reaction with $AgNO_3$).

A quantity of 65 g of $\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}$ was dissolved in distilled water, and a few drops of 2 mole·L^{-1} HNO_3 were added preventing partial hydrolysis of uranyl nitrate. This solution was passed through the column at a rate of approximately 0.5 mL/minute. Then, the column was washed with 250 mL of distilled water. UO_2^{2+} ions were eluted with 0.5 mole·L^{-1} HCl at a rate of 0.5-0.6 mL/minute, until the effluent was free of UO_2^{2+} ions (negative reaction with $K_4[\text{Fe(CN)}_6]$). The column was washed once more with distilled water until Cl^- ions were absent in the effluent. Thorium (UX_1 radionuclide) ions were eluted with 5% oxalic acid solution until the β^- radioactivity became negligible in the effluent (with approximately the same magnitude with the natural background).

The global repartition coefficient of UX_1 radionuclide between aqueous phase and organic phase were determined using an ultra diluted radionuclide aqueous solution, containing approximately 0.1 mole·L^{-1} oxalic acid and different concentrations of NaF, respectively, NaH_2PO_4 and an organic solution of tributylphosphate in benzene (20% v/v).

In various 50 mL separatory funnels there were put 10 mL organic phase and 10 mL aqueous phase containing either NaF (concentration varying between zero and $8\cdot10^{-4}$ mole·L^{-1}) or NaH_2PO_4 (concentration varying from zero to $12\cdot10^{-3}$ mole·L^{-1}). All the others components were maintained at the same concentrations. The separatory funnels were shaken vigorously for 2 minutes each. Then, they were placed for 60 minutes in a thermostat at 25 °C. During heating, the funnels were shaken for 2 minutes at 10 minutes of break. In the end the separatory funnels were left to rest for 15 minutes, the time on which the phases have become separated completely. From every separatory funnel 3 aliquots of 2 mL were extracted, and the specific radioactivity was determined for each sample. The mean value of activity was calculated, allowing the evaluation of the mean specific activity

expressed in impulse/minute·mL for every separation system. The mean values have been considered as the specific activities of aqueous phases, when the repartition equilibrium was reached. At equilibrium, organic phase activities were obtained by difference between initial activity and the value found for aqueous phase. Global distribution coefficient, for each system, was calculated as ratio between the activities for organic and aqueous phases.

Results and discussions

In Tables 1 and 2 experimental results on the extraction of $^{234}_{90}Th^{4+}$ from aqueous solutions containing F^- and H_2PO_4, respectively, are presented.

Table 1. Global distribution coefficients for $^{234}_{90}Th^{4+}$ at various F^- concentrations in aqueous phase.

Nº	$^{234}_{90}Th^{4+}$ volume (mL)	NaF 10^{-3} mole·L^{-1} volume (mL)	Dist. water volume (mL)	Aq. phase activity ipm/mL	Org. phase activity ipm/mL	Global distribution coefficient P_j	$logP_j$	[NaF]·10^5 (mole·L^{-1})	log[NaF]
1	2.0	0.0	8.0	1044	3341	3.200	0.505	0	-
2	2.0	0.1	7.9	1401	2984	2.129	0.328	1	-5.000
3	2.0	0.2	7.8	1693	2692	1.590	0.201	2	-4.699
4	2.0	0.3	7.7	1932	2453	1.269	0.104	3	-4.523
5	2.0	0.4	7.6	2139	2246	1.050	0.021	4	-4.398
6	2.0	0.5	7.5	2313	2072	0.896	-0.048	5	-4.301
7	2.0	0.6	7.4	2463	1922	0.780	-0.108	6	-4.222
8	2.0	0.8	7.2	2712	1673	0.617	-0.209	8	-4.097
9	2.0	1.0	7.0	2906	1479	0.509	-0.293	10	-4.000
10	2.0	2.0	6.0	3472	913	0.263	-0.580	20	-3.699
11	2.0	4.0	4.0	3898	487	0.125	-0.903	40	-3.398
12	2.0	6.0	2.0	4071	314	0.077	-1.113	60	-3.222
13	2.0	8.0	0.0	4164	221	0.053	-1.276	80	-3.097

The dependence between the global distribution coefficient and the ligand concentrations in the aqueous phase is plotted in Figures 1 and 2 for the experiment with fluoride and dihydrogenphosphate, respectively.

Table 2. Global distribution coefficients for $^{234}_{90}Th^{4+}$ at various $H_2PO_4^-$ concentrations in aqueous phase.

Nº	$^{234}_{90}Th^{4+}$ volume (mL)	NaH$_2$PO$_4$ 10^{-3} mole·L^{-1} volume (mL)	Dist. water volume (mL)	Aq. phase activity ipm/mL	Org. phase activity ipm/mL	Global distribution coefficient P_j	$logP_j$	[NaH$_2$PO$_4$] ·10^3 (mole·L^{-1})	log[NaH$_2$PO$_4$]
1	2.0	0.0	8.0	943	3119	3.20	0.505	0	-
2	2.0	0.5	7.5	1054	2908	2.76	0.441	1	-3.000
3	2.0	1.0	7.0	1165	2797	2.40	0.380	2	-2.699
4	2.0	1.5	6.5	1278	2684	2.10	0.322	3	-2.523
5	2.0	2.0	6.0	1390	2572	1.85	0.267	4	-2.398
6	2.0	2.5	5.5	1501	2461	1.64	0.215	5	-2.301
7	2.0	3.0	5.0	1611	2351	1.46	0.164	6	-2.222
8	2.0	4.0	4.0	1817	2145	1.18	0.072	8	-2.097
9	2.0	6.0	2.0	2189	1773	0.81	-0.092	12	-1.921

The relationship between global distribution coefficient, P_j, ligand concentration in aqueous phase, $[L_j]$ and global stability constants, β_i, for the complex species that are formed by radionuclide with ligand, is similar with the equation obtained in the case of radionuclide distribution between an aqueous phase and a solid ions exchanger, at various concentration of ligand in aqueous phase [6,7]:

$$\frac{P_0 - P_j}{P_j} = \sum_{i=1}^{n} \beta_i [L_j]^i \qquad (2)$$

where P_0 is the global distribution coefficient in the absence of the ligand and n is the maximum coordination number of the given radionuclide. For the computation of n stability constants, i.e. $\beta_1, \beta_2 \dots \beta_n$, it was formed a n order system consisting of n type (2) equations in which the concentrations of ligand in aqueous phase are $[L_j]$ ($1 \leq j \leq n$) and P_j is the corresponding global repartition coefficient. The solutions of this equation system are the n stability constants, $\beta_1, \beta_2 \dots \beta_n$. To increase the evaluation precision there were constituted 6 systems of n equations, using the values from the Tables 1 and 2. These systems were solved using adequate mathematical approach, 6 values for each constant of stability were obtained. The mean values of stability constants were determined accompanied by the proper mean deviation.

The radionuclide ions, $_{90}^{234}\text{Th}^{4+}$, forms with F^- anionic ligand three cationic complex species: $[\text{ThF}]^{3+}$, $[\text{ThF}_2]^{2+}$ and $[\text{ThF}_3]^+$. With H_2PO_4^- anion, two complex species are formed: $[\text{Th}(\text{H}_2\text{PO}_4)]^{3+}$ and $[\text{Th}(\text{H}_2\text{PO}_4)_2]^{2+}$. In salting out processes, others complex combinations, with higher coordination numbers, can appear at very high anion concentration [9÷12]. The stability constants values corresponding to the complex species formed by radionuclide ions, $_{90}^{234}\text{Th}^{4+}$ with F^- and H_2PO_4^- ligands are shown in table 3.

Table 3. Total stability constants of the complex species formed by $^{234}\text{Th}^{4+}$ radionuclide with the F^- and H_2PO_4^- anionic ligands

Nº	Total stability constant β_i	Anionic ligand	
		F^-	H_2PO_4^-
1	β_1	$(5.12 \pm 0.43) \cdot 10^4$	$(1.50 \pm 0.03) \cdot 10^2$
2	β_2	$(2.85 \pm 0.25) \cdot 10^7$	$(7.96 \pm 0.12) \cdot 10^3$
3	β_3	$(9.32 \pm 0.48) \cdot 10^8$	-

As we have shown in previous paper [6] that the β_i values for all foreseen species allow to evaluate the chemical speciation, at a given value of ligand concentration, $[L]$, for studied radionuclide in aqueous phase. We can calculate the fraction of radionuclide that is contained in a given form $[MeL_i]$ with:

$$\alpha_i \ (\%) = \frac{\beta_i}{\sum_{j=0}^{n} \left(\beta_j [L]^{j-1}\right)} \cdot 100 \qquad (3)$$

were α_i (%) is the fraction (in percents), from the total quantity of radionuclide, that can be found in a given chemical form at a certain concentration of ligand in aqueous phase. Thus, for a constant concentration of ligand in aqueous phase, each species present specific fractions of total radionuclide concentration. In aqueous phase at a monotone variation of ligand concentration, the α_i fractions attained a maximum value which corresponds to a certain concentration of ligand, $[L_i]_{max}$, when the concentration of that specie is maximum. The expressions for $[L_i]_{max}$ and α_i^{max} are [8]:

$$[L_i]_{max} = \sqrt{\frac{\beta_{i-1}}{\beta_{i+1}}} \tag{4}$$

and:

$$\alpha_i^{max} = \frac{\sqrt{\dfrac{\beta_i^2}{\beta_{i-1} \cdot \beta_{i+1}}}}{2 + \sqrt{\dfrac{\beta_i^2}{\beta_{i-1} \cdot \beta_{i+1}}}} \tag{5}$$

With (4) and (5) it can be calculated the chemical speciation for $^{234}_{90}\text{Th}^{4+}$ radionuclide in aqueous solutions, at various values of F^- and $H_2PO_4^-$ inorganic ligand concentrations. In Figures 1 and 2 the variation in the chemical speciation of $^{234}_{90}\text{Th}^{4+}$ in the presence of various concentration of F^- and $H_2PO_4^-$, respectively, are presented.
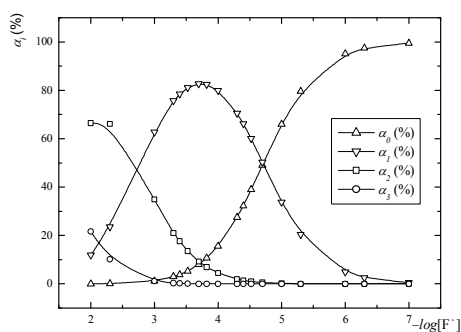

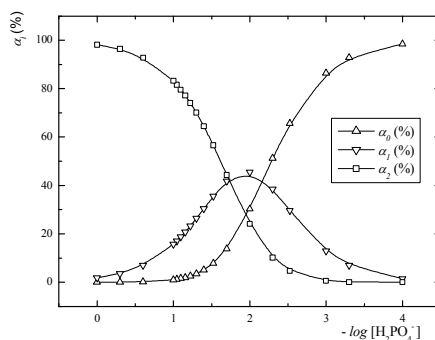**Fig. 1**: *Thorium chemical speciation at different F⁻ concentrations.*

Fig. 2: *Thorium chemical speciation at different $H_2PO_4^-$ concentrations.*

Form these data it can be noticed that ^{234}Th radionuclide forms in aqueous environment various compounds containing anionic ligands (F^- or $H_2PO_4^-$) even at very low concentrations of ligand, approximately 10^{-7} mole·L^{-1}. However, this behaviour may be revealed significantly only at concentrations above 10^{-6} mole·L^{-1}, when the $[ThF]^{3+}$ specie has a rate of almost 5%, and reaches a maximum of 83% at $2\cdot10^{-4}$ mole·L^{-1}. These experimental values are in a good agreement with those obtained from theoretical evaluation by equations (4) and (5): $[\alpha_1^{max}]$ = 82.7% and $[F_1^-]^{max}$ = 1.87·10^{-4} mole·L^{-1}. $[ThF_2]^{2+}$ specie present a significant rate only at F^- concentration exceeding 10^{-4} mole·L^{-1}. $[ThF_3]^+$ is the single specie that exists at concentrations above 1 mole·L^{-1}.

In the case of $H_2PO_4^-$ ligand, complex combinations are formed at higher concentrations, about 10^{-4} mole·L^{-1}. $[Th(H_2PO_4)]^{3+}$ specie has the maximum quantity, circa 45%, at a $[H_2PO_4^-]$ concentration of about 10^{-2} mol·L^{-1}. At this concentration all species existent in solution have almost the same rate. The values calculated are, in a good agreement with the experimental assessment. $[Th(H_2PO_4)_2]^{2+}$ is the only specie that exists at concentrations of ligand above 0.5 mole·L^{-1}.

Conclusions

The distribution study of $^{234}_{90}$Th^{4+} between ultradiluted radionuclide aqueous solutions and benzene phase at various ligand concentrations may be applied in the determining of **chemical speciation** corresponding to radionuclide states in aqueous solution. This information can be applied for obtaining a high yield in the efficient extraction of ^{234}Th radionuclide from aqueous solutions. Thus, this method has great importance for the radiochemical depollution of low activity residual waters resulted from nuclear technologies, before they are spread in the environment.

REFERENCES

1. Anderson, S., Ekberg, C. and Foreman, M.R.S. (2003) Solvent Extr. and Ion Exch., 21 (5), 611.

2. Glaus, M. A., Hummel, W. and Van Loon, L.R., (2000) Appl. Geochem., <u>15</u>, 953.

3. Wenming, D., Hongxia, Z. and Meide, H., (2002) Appl. Radiat. Isot., <u>56</u>, 959.

4. Jones, M. N. and Bryan, N. D., (1998) Adv. Coll. Interface Sci., <u>78</u>, 1.

5. Iliescu, M., Podină, C. and Mandravel, Cr., (2002) Analele Universității București – Chimie, <u>XI</u>, 69.

6. Iliescu, M., Podină, C. and Jujea, Cr., (2003) Rev. Roumaine Chim., <u>48</u> (<u>11</u>), 853.

7. Iliescu, M., Jujea, Cr. and Podină, C., (2004) Analele Universității București – Chimie, <u>XIII</u>, 219.

8. Iliescu, M., Podină, C. and Jujea, Cr., (2004) Rev. Roumaine Chim., <u>49</u> (<u>11</u>), 943.

9. Seaborg, G. T. and Katz, J. J., (1957) <u>The Chemistry of the Actinide Elements</u>, Ed. J. Wilei & Sons INC, NewYork, 64-68.

10. Spacu, P., Stan, M. and Gheorghiu, C., (1978) <u>Tratat de Chimie Anorganică</u>, vol. III, Ed. Tehnică, București, 735-738.

11. Neck, V., Müller, R. and Bouby, M., (2002) Radiochem. Acta, <u>90</u>, 485.

12. Östhols, E., Bruno, J. and Grenthe, I., (1994) Geochim. Cosmochim. Acta, <u>58</u>,613.