

THE IMPORTANCE OF COMPLEXES OF PLUTONIUM AND AMERICIUM WITH

INORGANIC ANIONS PRESENT IN NATURAL WATERS

A. AVOGADRO, G. BIDOGLIO and C.N. MURRAY

Commission of the European Communities, Joint Research Centre,
Ispra Establishment, I-21020 Ispra (Varese), ITALY

Resumé

La formation de complexes avec les anions présents dans les eaux naturelles a une grande importance sur la distribution des éléments transuraniens dans l'environnement. Parmi les différents agents complexants, les ions carbonates-bicarbonates jouent un rôle prépondérant.

Cette communication présente les résultats d'une étude théorique et expérimentale menée au centre de recherche d'Ispra afin de mieux comprendre la nature des différentes espèces solubles potentiellement présentes dans les eaux naturelles.

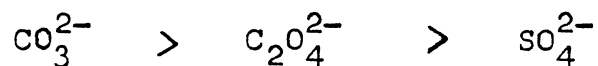
Abstract

This paper presents the results of theoretical and experimental studies performed in order to better understand the nature of soluble forms of transuranic nuclides in natural waters.

Information on physical and chemical state of transuranic elements in the aquatic environment is absolutely essential for an evaluation of their migration potential in aquatic systems. Despite the obvious need for an understanding of the environmental chemistry of these radionuclides, little information has been published on this subject.

In our studies, in order to define theoretically the nature of soluble transuranic species in natural waters, we used available thermodynamic data in order to calculate " α -factors"; when data were not available, the best possible estimate were made. The " α -factor" is defined as the ratio of the concentration of all the soluble forms for a given oxidation state, to the concentration of the free uncomplexed ion.

From informations available on complex formation of plutonium with inorganic ligands present in natural waters, complexes with carbonate ions are considered to be the most stable /1/, /2/. When carbonates are present, complex formation with other anions often becomes negligible. Unfortunately, precise data are not yet available or are not reliable. No quantitative data are for instance available on carbonate complexes of Pu (III); further the value of stability constant reported for Pu (IV) is certainly not correct. For Pu (III) the stability constant has been estimated by comparison with oxalate complexes. It is commonly accepted that the complexing power of the anions of dibasic acids toward plutonium follows the order



As values of the constants for oxalate complexes of Pu (III) and Pu (VI) are known, we have assumed that stability constant of carbonate complexes are at least similar or even greater. We have adopted literature values for di-carbonate and oxalate complexes of Pu (III) and (VI), (Table 1). By simple proportion the stability

constant K_2 of Pu (III) di-carbonate complex has been calculated to be $7 \cdot 10^{12}$.

Table 1 : Stability constants for di-oxalate and di-carbonate complexes of Pu (III) and Pu (VI)

di-oxalate		di-carbonate	
Pu (III)	Pu (VI)	Pu (III)	Pu (VI)
$2 \cdot 10^9$	$2.9 \cdot 10^{11}$	---	10^{15}

On the basis of similar arguments, the stability constants for mono and tri-carbonate complexes of Pu (III) have been calculated to be $K_1 = 3.6 \cdot 10^9$ and $K_3 = 1.4 \cdot 10^{16}$. These values have then been used for " α -factor" determination. It is obvious however that an experimental verification will be necessary.

For Pu (IV) the only experimental value found in the literature for the stability constant of carbonate complex was reported to be 10^{47} . This value has to be rejected because it would lead to unacceptable conclusions concerning the solubility of plutonium. For instance, in a natural system in equilibrium with atmospheric CO_2 , the carbonate concentration would be sufficient to avoid any precipitation of $\text{Pu}(\text{OH})_4$ due to the fact that the remaining "free" plutonium would not be sufficient to reach the solubility product of the hydroxide.

The stability constant of Pu (IV) carbonate complex has therefore been treated as a variable parameter in order to demonstrate

its influence on governing the predominance region of the different plutonium species.

We have developed, for this purpose, a computer code to calculate " α -factors" and to assess the plutonium distribution among the different species and oxidation states. The results of this parametric study, for the groundwater condition, are shown in Figures 1 to 3.

From the figures it is apparent that if K (IV) (stability constant of Pu (IV) carbonate complex) exceeds a given value which depends on Eh and pH, the Pu (IV) carbonate complex could become the only important species, both in reducing (Eh = 0,15 Volts, Figure 1) as well as in oxidizing conditions (Eh = 0,6 Volts, Figure 2). This fact is further illustrated in Figure 3 where, at pH = 8 the region of stability of different plutonium oxidation states are shown as a function of Eh. The dashed zone represents the coexistence region where the different carbonate complex concentrations differ by no more than one order of magnitude.

It may be seen that for sufficiently high values of K (IV), Pu (IV) can predominate over the entire range of environmental redox potentials ; for low K (IV) values, either Pu (III) or Pu (VI) are the species of major importance depending upon the reducing or oxidizing conditions of the system. The theoretical conclusion that plutonium should be in the Pu (VI) oxidation state in sea water (pH = 8,1 ; Eh = 0,729) fits well with the experimental observation of Nelson and Lovett /3/ in the eastern Irish Sea, under the influence of discharges of the Windscale nuclear fuel reprocessing plant.

In view of the importance of having a better understanding the exact value of stability constants of carbonate complexes for the various oxidation states of transuranics, an experimental programme has been started at the J.R.C. Ispra. This programme aims to identify the forms of the complexes produced and their respective stability constants. This study has been initiated using Europium

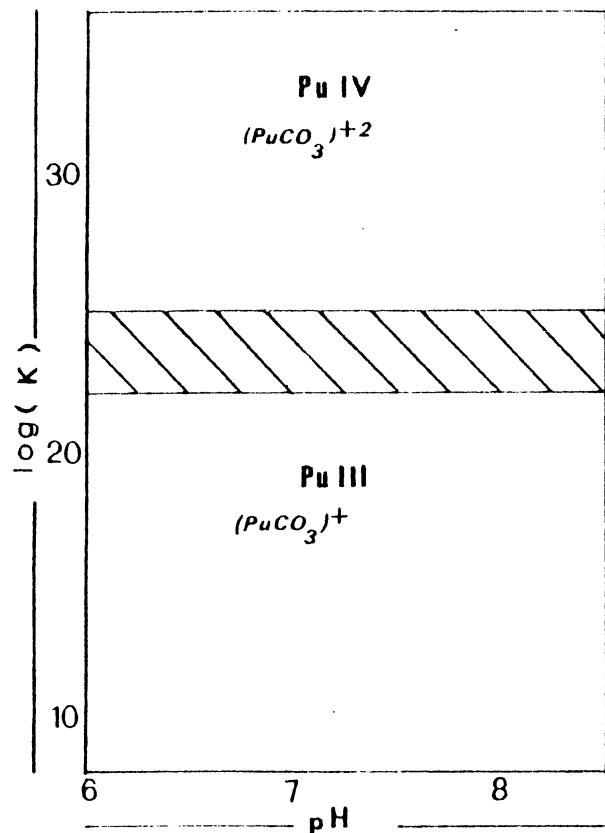


Figure 1

Plutonium distribution between (III) and (IV) states as a function of K (IV) and pH in reducing conditions :

$$Eh = 0,150 \text{ V}$$

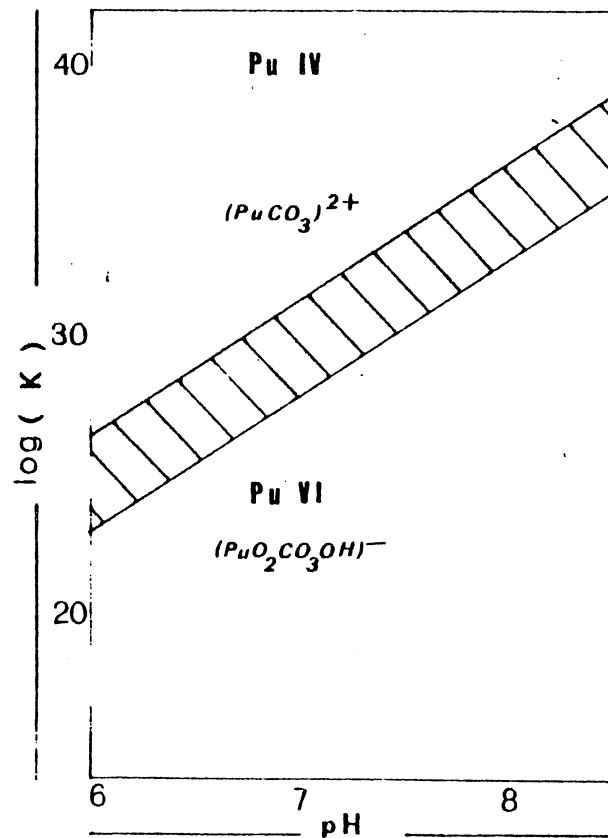


Figure 2

Plutonium distribution between (IV) and (VI) states as a function of K (IV) and pH in oxidizing conditions :

$$Eh = 0,60 \text{ V}$$

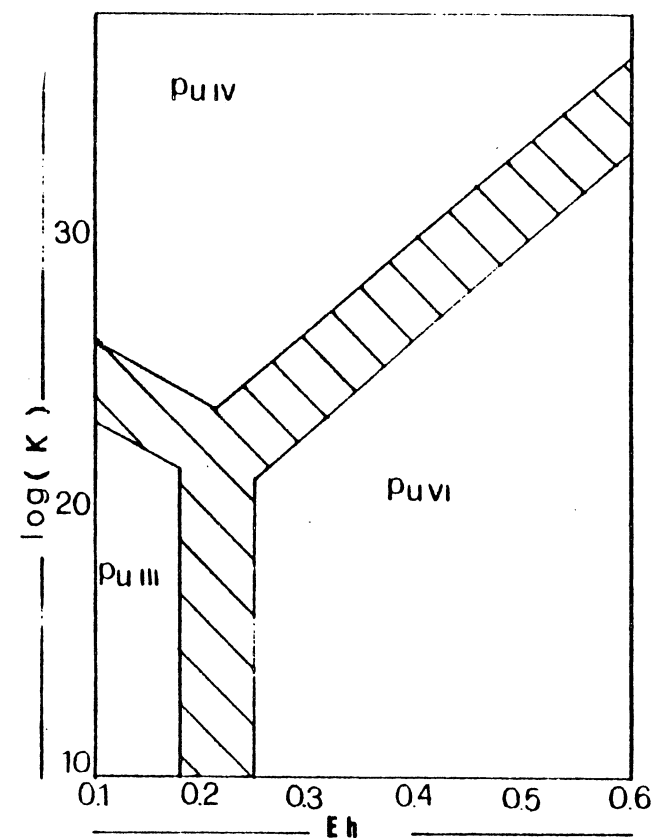


Figure 3

Stability regions of (III), (IV) and (VI) plutonium states as a function of Eh and K (IV) at $pH = 8,0$

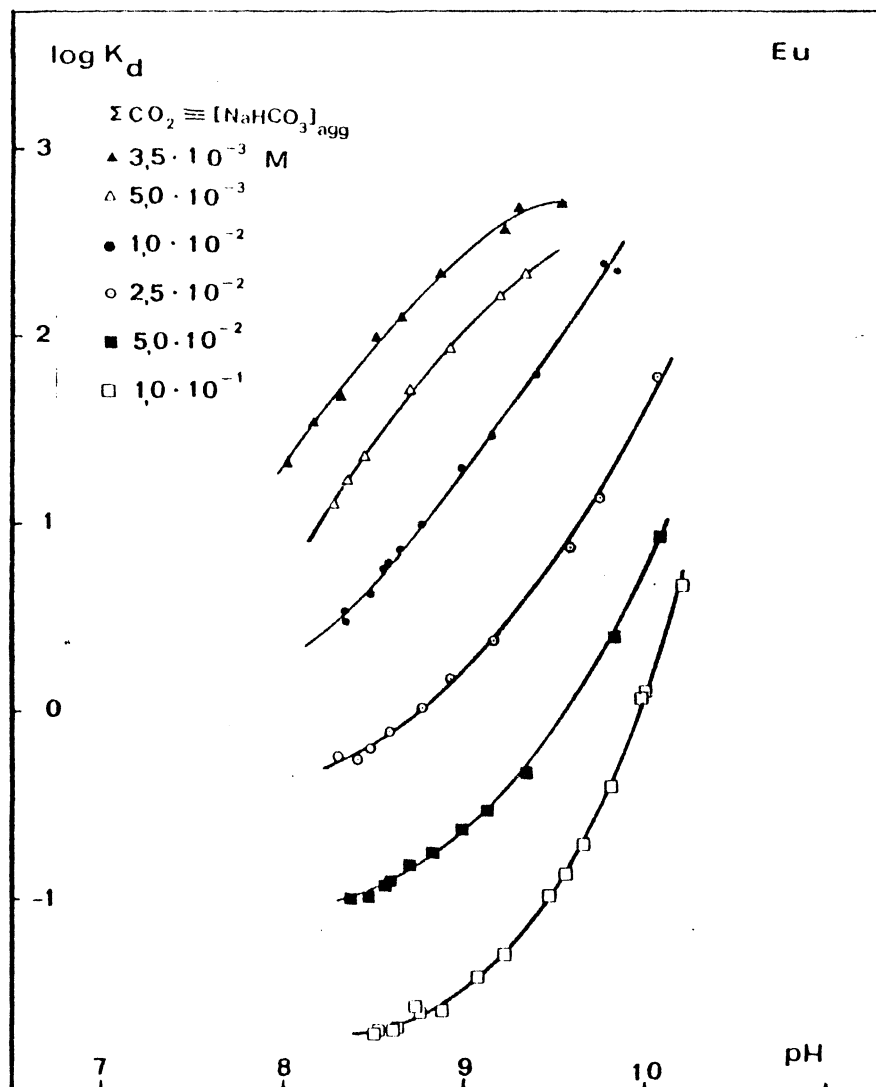


Figure 4 : Distribution coefficient at 22°C of $^{152+154}\text{Eu}$ at various concentrations of NaHCO_3 (ΣCO_2) as a function of pH organic phase = 1,3 diphenyl, 1,3 propandyon $5 \cdot 10^{-2}$ M in benzene

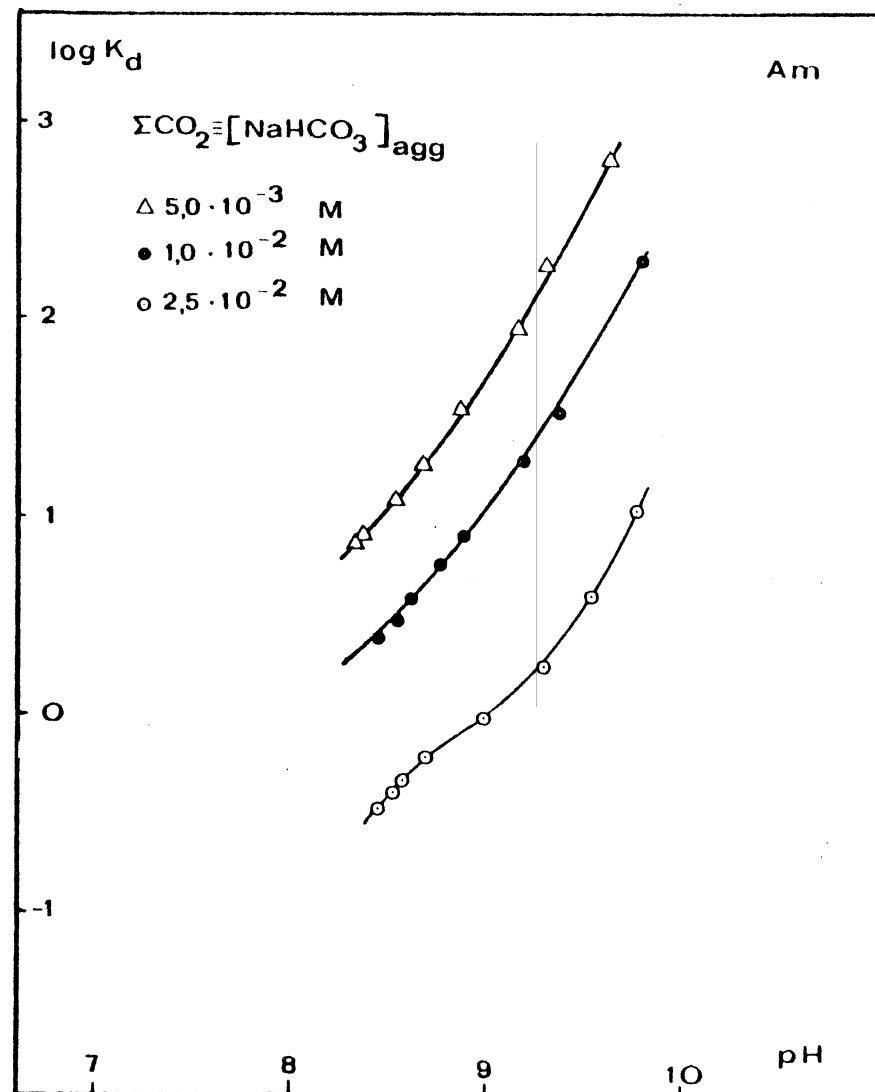
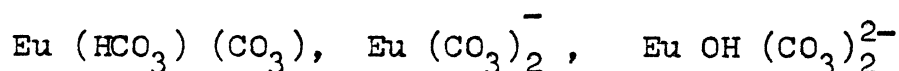


Figure 5 : Distribution coefficient at 22°C of ^{241}Am (III) at various concentrations of NaHCO_3 (ΣCO_2) as a function of pH. Organic phase as in Figure 4

as an analogue of the actinides. Spectrofotometric and electrochemical techniques suitable in general for the direct study of equilibria in solutions are not applicable in this case because of the very low experimental concentration (10^{-9} M) ; the methods of liquid-liquid extraction with radioactive tracers have thus been adopted. The complexing effect is indicated by the lowering of the distribution coefficient (K_d), as bicarbonate concentration is increased in solution (Figure 4). The interpretation of these experimental data is undertaken using a mathematical model derived by the Scandinavian School /4/ and further developed by R. Guillaumont /5/. The present study /6/ has demonstrated that in conditions similar to those found in groundwaters, soluble Europium is present in the form of anionic complexes of the type :



As the pH raises, the relative percentage of the forms above increase in the order shown, being highest for $\text{Eu OH}(\text{CO}_3)_2^{2-}$. The derived stability constants are respectively

$$2,61 \cdot 10^6, \quad 7,95 \cdot 10^7, \quad 3,33 \cdot 10^{12}$$

Analog studies have been initiated with americium (Figure 5) and preliminary observation indicate the presence of anionic species similar to those found with Europium.

The present theoretical considerations, clearly indicate the need for more detailed laboratory studies to investigate thermodynamic and kinetic aspects of the environmental behaviour of transuranic nuclides.

REFERENCES

- /1/ A.D. Gel'man, A.I. Moskvina, L.M. Zaitsev, M.P. Mefod'eva, "Complex compounds of transuranium elements" 1962, Consultants Bureau - New York
- /2/ A. Saltelli, A. Avogadro, G. Bertozzi "Assessment of plutonium chemical forms in groundwater" ; Proceedings of the Workshop on the migration of long-lived radionuclides in the geosphere, Brussels 29th-31st January, 1979 OECD-NEA Publications 1979
- /3/ D.M. Nelson, M.B. Lovett ; Nature 276, 599 (1978)
- /4/ J. Rydberg, Arkiv för Kemi, 8, 101 (1955)
- /5/ R. Guillaumont, R. Muxart, G. Boussières ; Bull. Soc. Chim. 5, 1952 (1968)
- /6/ G. Bidoglio, B. Marcandalli, I.R. Bellobono ; "Determinazione delle costanti di stabilità di carbonato - complessi di lantanoidi", Convegno Nazionale di radiochimica e chimica nucleare, Padova 12-14 Maggio 1980 (in press).

AVOGADRO, A., BIDOGLIO, G., MURRAY, C.N.

"The importance of complexes of plutonium and americium with inorganic anions present in natural waters"

Paper presented by A. Avogadro (Italy)

Discussion

No comment.