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By Lionel Bion[1],*, Eric Ansoborlo[2], Valérie Moulin[3], Pascal Reiller[1], Richard Collins[4], Rodolphe Gilbin[5], Laureline Février[5], Thomas Perrier[5], Frank Denison[5] and Gérard Cote[6]

[1] CEA Saclay – DEN/DPC/SECR/LSRM, Bât. 391, 91191 Gif sur Yvette Cedex, France
[2] CEA Marcoule – DEN/DRCP/CETAMA, Bât.181, 30207 Bagnols sur Cèze, France
[3] CEA Saclay – DEN/DDIN, Bât. 121, 91191 Gif sur Yvette Cedex, France
[4] CEA Saclay – DSM/DRECAM/LPS, 91191 Gif sur Yvette Cedex, France
[5] IRSN – DPRE/SERLAB/LRE, Centre de Cadarache, 13115 Saint-Paul-les-Durance, France
[6] ENSCP, 11 rue Pierre et Marie Curie, 75005 Paris, France

Speciation / Thermodynamic database / Equilibrium constant / Americium(III)

Summary. An intercomparison exercise was led in order to study the impact of thermodynamic database (TDB) on the speciation of americium(III) in biochemical media.

A first exercice was led, considering only the americium(III) species in solution. Even with different data sets, all the exercises are in relatively good agreement, concluding to successive complexation of the radioelement by phosphate (pH range from 0 to 3), citrate (pH range from 3 to 8) and hydroxo-carbonate (pH range from 8 to 14). Nevertheless, the speciation of americium differs for each pH range from one work to an other.

These results are still observed when the speciation calculation includes the formation of solids. Nevertheless, some workers did not integrate in their data set the formation constant of $Am(PO_4)$. This solid is known to be very insoluble in typical biological media. All the calculations where $Am(PO_4)$ was not in the TDB presented a speciation where americium is solvated (mostly under citrate forms). When the formation of $Am(PO_4)$ is considered, the actinide is quantitatively present under this solid species.

This work is a representative example of the impact of the thermodynamic data used in speciation exercises. Some exercices, using uncompleted TDB had wrong results and led to the conclusion of the necessity in the use of expertised and extended TDB.

Introduction

Existing thermodynamic database (TDB) can be critical reviews [1, 2], where only certified values are present (but important species without certification are still missing) or exhaustive compilations without certification [8].

On the last years, some new "extended" TDB, with expertise work but including more than certified values are now available [5–7]. These "extended" TDB allow to obtain realistic modelisation of the speciation, using a more "complete" set of data. Unfortunately, they are not systematically used in calculations, leading to erroneous modelisation of speciation.

Since 2002, the CETAMA work group "GT32" has organized modelisation exercises were contributors can propose their modelisation for the speciation of a given element in a specific medium, using their own TDB and speciation code. The aim of this work is to define the potential missing data and errors in the modelisation of the speciation, especially when using the existing TDB.

Description of the intercomparison exercise

The composition of the simplified biological media was chosen as presented in Table 1 and used for all the speciation calculations. One exercise consists in the determination of speciation diagrams (concentration of americium species *versus* pH): speciation without precipitation and speciation including precipitation. Five exercises were carried out.

Each contributor had to modelise the speciation of trace amount of americium(III) as function of acidity, including or not the precipitation reaction. Each worker used his own set of thermodynamic data and calculation code (presented in Table 2). It is important to note that, for all the modelisation, the Am(III)–hydroxide–carbonate system was described using NEA data [1, 2]. Each contributor used dif-

Table 1. Composition of the simplified biological media used in the modelisation exercise. Total carbonate concentration was maintained to 25 mM in solution.

$[Am]_{tot}$	1 µM
$[Cl]_{tot}$	0.1 M
$[Na]_{tot}$	0.1 M
$[PO_4]_{tot}$	1 mM
$[CO_3]_{tot}$	25 mM
$[Citrate]_{tot}$	0.1 mM

*Author for correspondence (E-mail: bion@cea.fr).

Table 2. Sets of thermodynamic data and speciation codes used in the modelisation exercise.

		ex 1	ex 2	ex 3	ex 4	ex 5
Inorganic complexation	$Am^{3+} + H_2O = AmOH^{2+} + H^+$			-7.2 ± 0.5 [1, 2]		
	$Am^{3+} + 2H_2O = Am(OH)_2^+ + 2H^+$			-15.1 ± 0.7 [1, 2]		
	$Am^{3+} + 3H_2O = Am(OH)_3(aq) + 3H^+$			-26.2 ± 0.5 [1, 2]		
	$Am^{3+} + CO_3^{2-} = AmCO_3^+$			8.0 ± 0.4 [1, 2]		
	$Am^{3+} + 2CO_3^{2-} = Am(CO_3)_2^-$			12.9 ± 0.6 [1, 2]		
	$Am^{3+} + 3CO_3^{2-} = Am(CO_3)_3^{3-}$			15 ± 1 [1, 2]		
	$Am^{3+} + Cl^- = AmCl^{2+}$			0.24 ± 0.03 [1, 2]		
	$Am^{3+} + 2Cl^- = AmCl_2^+$			-0.74 ± 0.05 [1, 2]		
	$Am^{3+} + H_2PO_4^- = AmH_2PO_4^{2+}$			3 ± 0.5 [1, 2]		
Organic complexation	$Am^{3+} + HCit^{2-} = AmHCit^+$	6.66 [8]	No value	No value	11.36 [9]	6.66 [8]
	$Am^{3+} + H^+ + 2Cit^{3-} = AmHCit(Cit)^{2-}$	No value	No value	No value	18.97 [9]	No value
	$AmCit + HCit^{2-} = AmH(Cit)_2^{2-}$	2.5 [8]	No value	No value	No value	2.5 [8]
	$Am^{3+} + 2Cit^{3-} = Am(Cit)_2^{3-}$	12.92 [8]	12.92 [8]	No value	14.29 [9]	12.92 [8]
	$Am^{3+} + Cit^{3-} = AmCit (aq)$	9.76 [8]	9.76 [8]	5.9 [10]	8.69 [9]	9.76 [8]
	$Am^{3+} + 2HCit^{2-} = Am(HCit)_2^-$	10.07 [8]	No value	No value	20 [9]	10.07 [8]
Solids	$Am^{3+} + 3H_2O = Am(OH)_3 (am) + 3H^+$			-16.9 ± 0.8 [1, 2]		
	$Am^{3+} + 3H_2O = Am(OH)_3 (c) + 3H^+$			-15.6 ± 0.6 [1, 2]		
	$Am^{3+} + CO_3^- + 1OH^- = AmCO_3OH (am)$			20.2 ± 1 [1, 2]		
	$Am^{3+} + CO_3^- + 1OH^- + 0.5H_2O$ $= AmCO_3OH \cdot 0.5H_2O (cr)$			22.4 ± 0.5 [1, 2]		
	$Am^{3+} + PO_4^{3-} = AmPO_4 (am)$	24.79 ± 0.6 [1, 2]	No value	24.79 ± 0.6 [1, 2]	24.79 ± 0.6 [1, 2]	No value
Auxiliary data	$1HCO_3^- + 1H^+ = CO_2 (aq) + H_2O$			6.349 ± 0.05 [1, 2]		
	$HCO_3^- = CO_3^{2-} + 1H^+$			10.337 ± 0.04 [1, 2]		
	$PO_4^{3-} + 1H^+ = HPO_4^{2-}$			2.14 ± 0.03 [1, 2]		
	$1HPO_4^{2-} + 1H^+ = H_2PO_4^-$			7.212 ± 0.013 [1, 2]		
	$1H_2PO_4^- + H^+ = H_3PO_4 (aq)$			12.35 ± 0.03 [1, 2]		
	$Cit^{3-} + H^+ = HCit^{2-}$	6.4 [8]	6.4 [8]	5.63 ($I = 0.1$) [10]	6.4 [8]	No value
	$Cit^{3-} + 2H^+ = H_2Cit^-$	11.2 [8]	11.2 [8]	9.99 ($I = 0.1$) [10]	11.2 [8]	11.2 [8]
	$Cit^{3-} + 3H^+ = H_3Cit (aq)$	14.3 [8]	14.3 [8]	12.92 ($I = 0.1$) [10]	14.3 [8]	14.3 [8]

ferent set of data concerning the americium(III)–citrate and americium(III)–phosphate systems.

Five speciation exercises were made, using a different TDB for each one. The calculations were made using two speciation codes: JCHESS [3] and PHREEQC [4] (see Table 2).

Modelisation of the speciation in solution (without precipitation)

A first exercise was led, considering only the americium species in solution. Considering that the total concentration of americium is 1 µM (higher than the solubilities of hydroxide solids or phosphate solids of the element), these calculations correspond to speciation in solution, normalized with total concentration in solution. For all these exercises, the speciation diagrams of americium(III) can be divided into three acidity ranges (Fig. 1).

For pH values inferior to 3: all the exercises agree with a strong complexation of americium by phosphate anions. Nevertheless, the set of data only includes NEA certified values [1, 2] concerning 1 : 1 complexes. Values concerning the complexes with higher stoichiometries, such as $Am(H_2PO_4)_x^{+3-x}$ ($x = 2$ to 4) [5, 6] are missing (no values concerning these species were mentioned in the critical review of NEA). The integration of these species would have led to the formation of phosphate complexes of americium on a larger pH range (near to neutral acidity values).
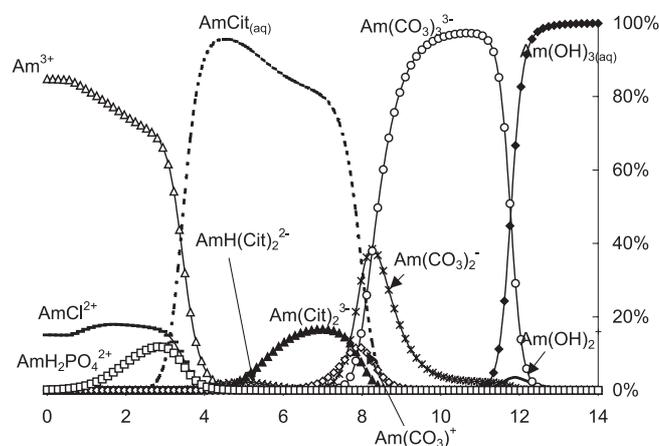

Fig. 1. Speciation diagram (as function of pH) of americium(III) without including precipitation reactions (calculation code Chess 3.04, see "exercise 5" in Table 2 for the set of thermodynamic data).

Concerning the pH range from 3 to 8, the speciation of americium corresponds to the formation of citrate complexes. Each exercise used its own set of data concerning the americium–citrate system, and a different type of complex appears in each calculation: $Am(Cit)^0$, $Am(HCit)^+$, $Am(HCit)(Cit)^{2-}$, $Am(Cit)_2^{3-}$ (see Table 1). Nevertheless, even if the nature of the predominant Am(III)-citrate complex differs, all the exercises lead to a quantitative citric speciation of americium in this pH range. Even with different thermodynamic data concerning the americium–citrate

system, all the contributors conclude that the speciation of americium in solution correspond to citric complexes species at physiological pH value (pH = 7.4).

For the pH values between 8 and 14, all the calculations agree with a speciation of americium with formation of carbonate and hydroxide complexes (Fig. 1). This is coherent with the use of identical data concerning the Am(III)–OH–CO_3 (Table 1).

To conclude about the modelisation of the speciation without including precipitation reaction, all the exercises agree with these three similar predominance: phosphate complexes (pH < 3), citrate complexes (3 < pH < 8), carbonate and hydroxide complexes (8 < pH < 14) (Fig. 1).

Modelisation of the speciation including precipitation reactions

All the comments presented in the previous paragraph are still valid in the case of the modelisation of the Am(III) speciation including precipitation equilibria. Nevertheless, the use of this species in the set of thermodynamic data is a key point for the calculations:

$$\log K\{Am^{3+} + PO_4{}^{3-} = AmPO_4 \text{ (am, hydr)}\} = 24.79 \pm 0.6 \text{ [5, 6]}.$$

If this data is present in the thermodynamic set of the exercise, the speciation diagram corresponds systematically to the quantitative formation of the solid for pH values between 3 and 12 (Fig. 2).

If the data concerning the solid $AmPO_4$ is missing, the speciation diagrams are similar to those obtained in the previous paragraph (without precipitation), except a sharp pH range where the hydroxycarbonate solid $Am(OH)(CO_3)$ appears (near pH = 8) (see Fig. 3).

The thermodynamic data concerning the solid species $AmPO_4$ is not certified in some extended database [7] but relatively certified [5, 6] and absolutely necessary to get a representative modelisation of the americium(III) speciation in biological media. Fig. 4, obtained for the pH value of
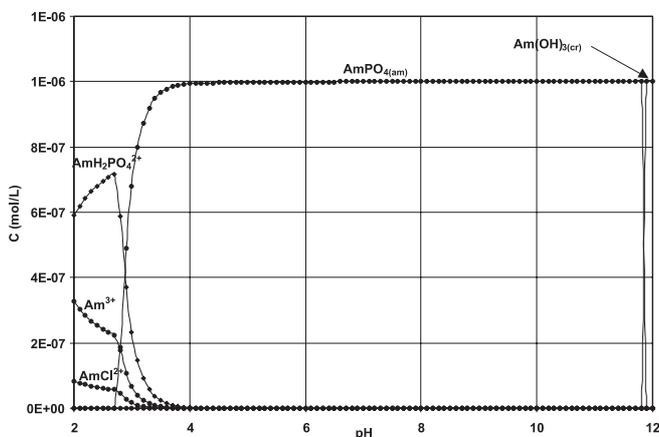
Fig. 2. Speciation diagram (as function of pH) of americium(III) including precipitation reactions (calculation code Chess 3.04, see "exercise 4" in Table 2 for the set of thermodynamic data). When using the data concerning the $AmPO_4$ solid specie, americium precipitate quantitatively from pH = 3 to pH = 14.
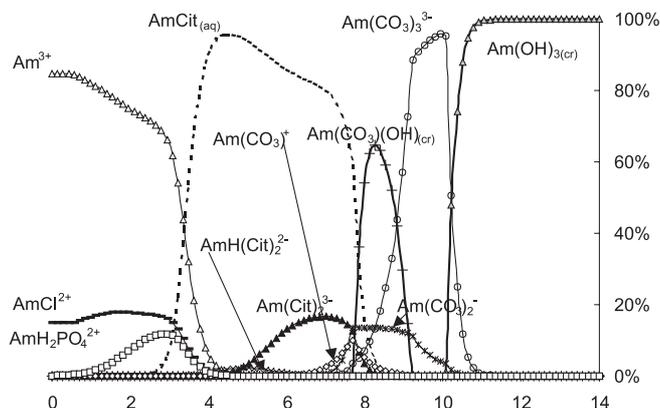
Fig. 3. Speciation diagram (as function of pH) of americium(III) including precipitation reactions (calculation code Chess 3.04, see "exercise 5" in Table 2 for the set of thermodynamic data). When the data concerning the $AmPO_4$ solid specie is missing, americium precipitate quantitatively from pH = 11 to pH = 14.
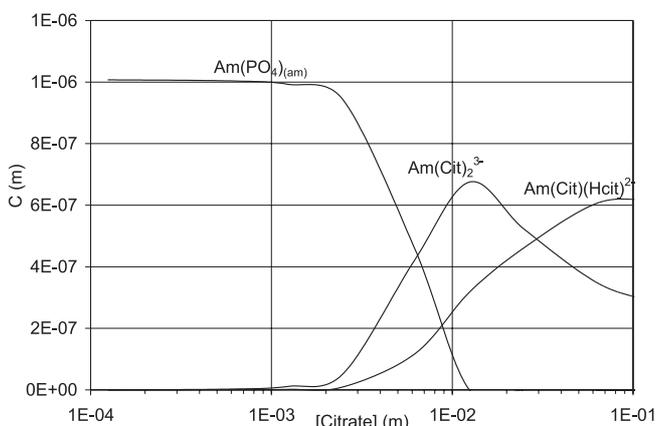
Fig. 4. Speciation diagram at pH = 7.4 (as function of total citrate concentration) of americium(III) including precipitation reactions (calculation code PHREEQC v2.6, see "exercise 4" in Table 2 for the set of thermodynamic data).

7.4 (physiological pH value of blood) demonstrates the stability of the phosphate solid, even at very high concentration of citrate ions (up to 0.01 M).

Conclusion

Modelisation of Am(III) speciation without formation of solid

Even if each user have used his own set of thermodynamic values and proposed different species, theses calculations led to a modelisation of the speciation of Am(III) in solution corresponding to citric complexes in the biological medium.

Modelisation of Am(III) speciation including formation of solid

In the opposite, the modelisation of the Am(III) speciation was different according to exercises. When the modelisations include $Am(PO_4)$, this solid appears to be the exclusive species of Am(III). When this precipitate is missing in the TDB, the modelisation of the speciation leads to complex

species of Am(III) in solution. We may assume that this modelisation is wrong and that the integration of the formation constant of this solid is absolutely necessary in the TDB.

References

1. Silva, R. J., Bidoglio, G., Rand, M. H., Robouch, P., Wanner, H., Puigdomenech, I.: *Chemical Thermodynamics 2: Chemical Thermodynamics of Americium*. NEA-OECD, Elsevier (1995).
2. Guillaumont, R., Fanghaenel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D. A., Rand, M. H.: *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, Technetium*. NEA-OECD, Elsevier (2003).
3. Van der Lee, J., De Windt, L: CIG-École des Mines de Paris Report LHM/RD/99/05.
4. Parkhurst, D.: US Geological Survey Report 95-4227.
5. Bion, L.: Radiochim. Acta **91**, 633 (2003).
6. Bion, L., Ansoborlo, E., You, D.: BASSIST, an extended thermodynamic database for radionuclide speciation calculations. Submitted to Radiochim. Acta.
7. Hummel, W., Berner, U., Curti, E., Pearson, F. J., Thoenen, T.: *NAGRA/PSI Chemical Thermodynamic Data Base 01/01*. Universal Publishers, Parkland, Florida (2002).
8. Powell, K. J.: *The IUPAC Stability Constants Database*. Academic Software, York, UK (1999).
9. Bouhlassa, S., Guillaumont, R.: J. Less Common Metals **99**, 157 (1984).
10. Wall, N., Borkowski, M., Chen, J. F., Choppin, G. R.: Radiochim. Acta **90**, 536 (2002).