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To cite this version:

Pascal E. Reiller, Thomas Vercouter, Lara Duro, Christian Ekberg. Thermodynamic data provided through the FUNMIG project: Analyses and prospective. Applied Geochemistry, 2011, 27 (2), pp.414-426. 10.1016/j.apgeochem.2011.09.011 . cea-00658296

HAL Id: cea-00658296

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Submitted on 16 Dec 2020

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Thermodynamic Data Provided Through the FUNMIG Project: Analyses and Prospective

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http://doi.org/10.1016/j.apgeochem.2011.09.011

Abstract

We are highlighting some of the needs for good quality thermodynamic data in radioactive waste management. A presentation of the thermodynamic data produced within the 6th framework integrated project FUNMIG (Fundamental processes of radionuclide migration) and how these works have helped in filling in relevant thermodynamic data gaps is given. The manuscript does not intend to be a complete review of thermodynamic data, but a short overview of the aqueous complexation of americium (III), lanthanides (III), uranium (VI), and thorium (IV) by sulphates, silicates, carbonates and phosphates. The work presented is based on the latest developments published in the literature and specifically addressed within the IP FUNMIG.

1. Introduction

The quality of thermodynamic data is one issue of relevance in different scientific and technical activities. Calculation of reaction yields, design of industrial processes, the development of protocols and processes in the pharmaceutical industry, mining activities, heating and cooling systems are some examples of activities where thermodynamic data are applied. The global nuclear cycle is not an exception where quality-assured thermodynamic data are needed (Voigt *et al.*, 2007). Many economic and intellectual resources have been invested in the determination of good quality thermodynamic data of the elements of interest for nuclear activities. From the preparation of the nuclear fuel itself, to the evolution of the different elements of a nuclear power plant, up to the final end of the spent nuclear fuel cycle, and products derived from its treatment after the discharge from the nuclear power plant reactor, research activities need good quality thermodynamic data. In the last years, nuclear waste management has been one of the disciplines where a larger quantity of efforts has been devoted to this type of research. Many nuclear waste management national agencies and related organisations have developed their own thermodynamic database for the elements of interest for nuclear waste management (Yui, 2001; Hummel *et al.*, 2002; Bion, 2003; Duro *et al.*, 2006).

The primary waste form resulting from nuclear energy production is spent nuclear fuel (SNF), but some national programs have chosen reprocessing. The most accepted concept for storage of either SNF or wastes from the reprocessing is currently its deep burial at several hundreds of meters underneath the surface in a geologically stable suitable host-rock, and isolated from the geological media by several engineering barriers based on material whose main function is to prevent the contact of the water either with the spent fuel or with the wastes (ANDRA, 2005a; ANDRA, 2005b). The use of good quality thermodynamic data is therefore an

important tool to evaluate the possible release of these radionuclides into the repository system, that is the near-field, and into the undisturbed geosphere, that is the far-field.

A typical composition of a sample of SNF after 38 years of its discharge from the reactor (inventory) is shown in Figure 1 (NIREX, 2002). Only those elements accounting for more of the 0.01% of the mass of the SNF are represented in the plot, from where the high amount of thermodynamic data of interest for the nuclear waste managers can be deduced. Many of the elements present in the waste, like actinide (An) elements, are not very common in other physico-chemical studies, so are the thermodynamic functions and data for these elements.

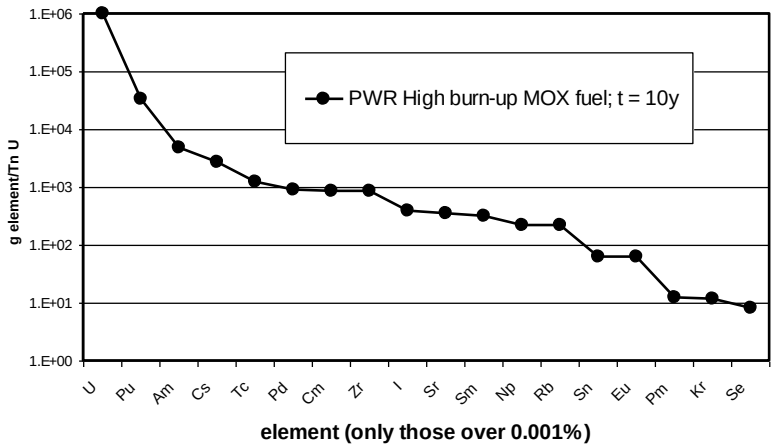

Figure 1. Example of inventory of a SNF (NIREX, 2002).

Since the beginning of the nineties, the Nuclear Energy Agency of the Organisation for the Economic Co-operation and Development (NEA-OECD) has commissioned panels of experts to provide reliable and internally consistent compilations of thermodynamic formation data ($\Delta_f G°_m$, $\Delta_f H°_m$, $S°_m$, and $C°_{p,m}$), reaction data and stability constants ($\Delta_r G°_m$, $\Delta_r H°_m$, $\Delta_r S°_m$, $\log_{10} K°$) (Wanner, 1991; Grenthe and Puigdomènech, 1997) for the nuclides involved in the nuclear cycle, *i.e.* uranium (Grenthe *et al.*, 1992), americium (Silva *et al.*, 1995), technetium (Rard *et al.*, 1999), neptunium and plutonium (Lemire *et al.*, 2001), selenium (Olin *et al.*, 2005), nickel (Gamsjäger *et al.*, 2005), zirconium (Brown *et al.*, 2005), thorium (Rand *et al.*,

2009) as well as organic complexes of some of theses metal ions (Hummel *et al.*, 2005). Important activity is devoted to updates with new data (Silva *et al.*, 1995; Guillaumont *et al.*, 2003). Much more than a catalogue of thermodynamic data and constants, these *Thermochemical Data Bases* publications (NEA-TDB reviews) provide an extensive and comprehensive scientific review of the information available in the scientific literature. The reviews are based both on data obtained from solution experiments as well as from calorimetric measurements and preferably supported by pieces of evidence of structure of the formed complexes whenever possible.

Considering the high level of expertise involved and the desired high quality of the selected thermodynamic data, these data selections inherently have inevitable justified gaps. In some cases, the raw data available in the literature are subject to critics or are not sufficiently documented as to be used by the expert panel. One illustrative example can be sought of in the first selection of thermodynamic data published for uranium (Grenthe *et al.*, 1992) where only an upper value for the formation of $UO_2(OH)_2(aq)$ was given. The same occurred with the selection of thermodynamic data for plutonium (Lemire *et al.*, 2001), where no cumulative formation constants for the Pu(IV) hydroxocomplexes ($Pu(OH)_n^{4-n}$, with $2 \leq n \leq 4$) were selected. Finally, one can also think about the solubility of $AmPO_4(s)$, which can be assessed using the corresponding Gibbs energy of the dissolution reaction, $\Delta_r G°_m$, given by Silva *et al.* (1995). But as no selected $\log_{10}K°$ value was present in the selection, substantial differences may appear in theoretical speciation calculations (Bion *et al.*, 2005). Subsequent updates of the thermodynamic data selection based on new experimental data – in the case of $UO_2(OH)_2(aq)$ – or deeper analyses of existing literature – in the case of $Pu(OH)_4(aq)$ – were able to partially fill in these gaps (Silva *et al.*, 1995; Guillaumont *et al.*, 2003). Nevertheless, one may note that there is still a need of experimental program in this field and data were recently reported (Neck *et al.*, 2007; Yun *et al.*, 2007).

The construction of applied thermodynamic databases of good quality is a task that will probably never end, although in the last years marked advances have been made thanks to the combination of different analytical techniques, molecular simulations and strategies for estimation of gaps in the available thermodynamic data. Management of uncertainties is also a matter of concern. Nevertheless, it is out of the scope of this paper and the reader is strongly encouraged to refer to expert views in the domain (Ekberg, 1999; Denison and Garnier-LaPlace, 2005).

Given the quality criteria of the review in Silva *et al.* (1995), only few data sets were available for extrapolation to zero ionic strength, and the authors called for more experimental data at other ionic strength values. In Guillaumont *et al.* (2003), spectroscopic data on Cm(III) were included in the data selection, assuming that the differences in comportment between americium and curium were smaller than the experimental uncertainties, and that spectroscopic data were less influenced by activity variations. The main differences are actually caused by relying on Cm(III) for evaluating Am(III) data, and some of them will be discussed in the present paper.

In natural media the main inorganic ligands are hydroxyl, carbonate, sulphate, silicate and phosphate. Contrary to the other ligands, phosphate is often not present in appreciable amount in deep groundwaters, except in ores or in living organism (Purvis *et al.*, 2004; Quiroz *et al.*, 2006), as in biofilms in granite environments. These ligands are accounted for in the critical reviews together with their auxiliary data. As an illustration of their importance, the theoretical repartition of soluble species of americium (III) using the last update of NEA selection (Guillaumont *et al.*, 2003) can be calculated using PHREEQC in an argillaceous water proposed by Gaucher *et al.* (2006) (Figure 2). Variation of carbonate concentration with pH is controlled via the solubility of Dolomite $(Ca,Mg)(CO_3)_2$. Given the number of possible complexes between pH 7 and 8.5, it is evident that accurate thermodynamic data are needed.

Furthermore, as a consequence of the aforementioned quality criteria of data and stoichiometry selection, one has to be assured that all the possible complexes are taken into account in theoretical calculation exercises.

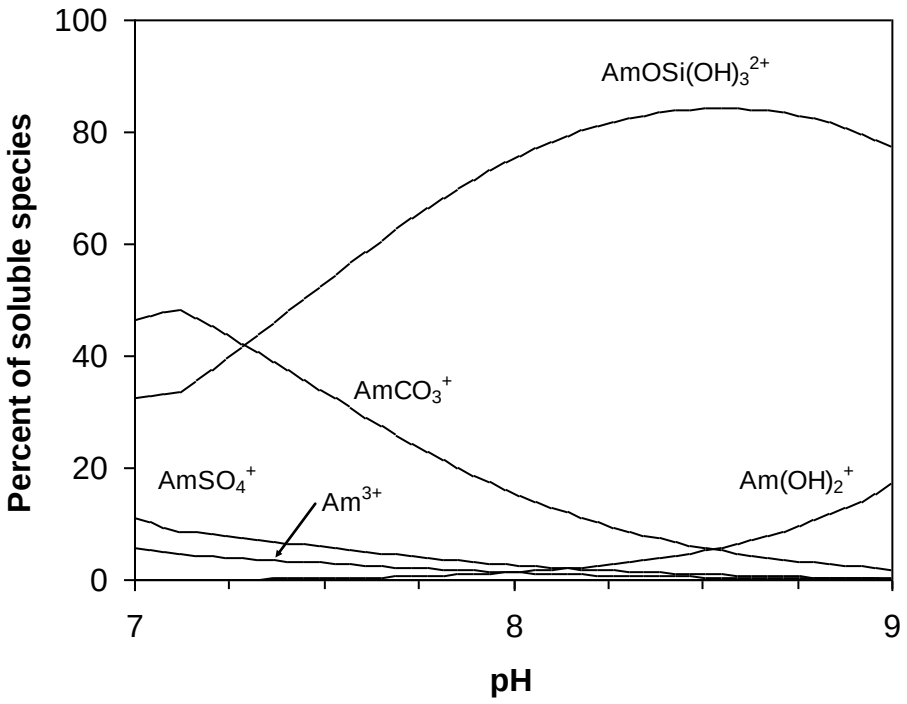

Figure 2. Percent of soluble species of americium(III) in equilibrium with $CaMg(CO_3)_2$ in an argillaceous water (Gaucher et al.*, 2006), calculated using the data from Guillaumont* et al. *(2003).*

Furthermore, the hydroxo, carbonate, and sulphate complexation of americium (III) was revised between the former (Silva *et al.*, 1995) and the latter selection (Guillaumont *et al.*, 2003) of NEA data. The visual results of the proportion of the hydroxo and carbonato complexes are reported in Figure 3 for the two selections at I = 1 mol/L using the specific ion interaction theory (Guillaumont *et al.*, 2003). Here the main difference lies in the decrease of the selected values for first and second hydrolysis constants. The high ionic strength used in Figure 3 helps in visualising the highly charged $Am(CO_3)_3^{3-}$ complex and its influence on the repartition of species. In the case of sulphate, selected values of complexation constants have

also been changed. This may have a significant impact on the speciation calculation, especially when sulphate is present at moderate concentration like in some groundwaters equilibrated with clays or if oxidation of pyrite occurs (Degueldre *et al.*, 2003; Beaucaire *et al.*, 2008; Gaucher *et al.*, 2009).

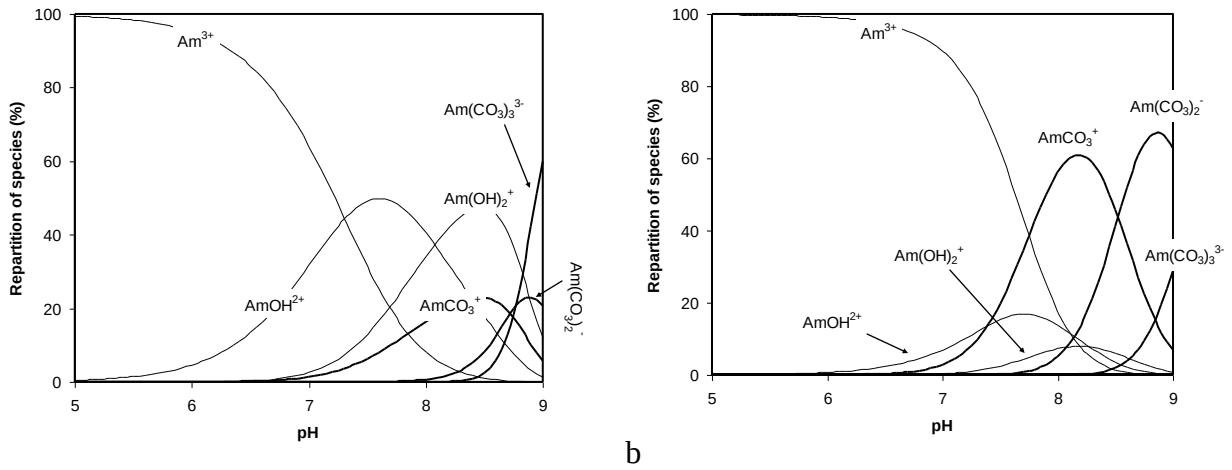

Figure 3. Differences induced in the speciation diagram of trace Am(III) at I *= 1 mol/L, and* $pCO_2 = 10^{-3.46}$ *atm, between values selected in Silva et al. (1995) (left) and Guillaumont et al. (2003) (right).*

Within the FUNMIG program, the first research and technological development component (RTDC-1) was dedicated to provide fundamental process knowledge and the required data for processes with comparably well established conceptual understanding. This included filling gaps or reducing apparent inconsistencies between thermodynamic data, which were the tasks of one work-package involving two teams: the Laboratory for the Speciation of Radionuclides and Molecules at the Commissariat à l'Energie Atomique (CEA, France) and the Department of Chemical and Biological Engineering at the Chalmers University of Technology (CTH, Sweden). From the expertise of these groups, and the other related programs within FUNMIG, it was proposed to focus the works on the speciation of trivalent lanthanides and actinides, and hexavalent uranium for the former group and on the phosphate complexation

of tetravalent thorium for the latter. Some elements studied were selected as proxies for other elements of interest but more difficult to handle in laboratory assays; europium (III) and thorium (IV) were used as analogues for the other trivalent actinides – *i.e.* Am(III) and Cm(III) – and tetravalent actinides – *i.e.* U(IV), Np(IV), and Pu(IV) –, respectively.

Furthermore, the effect of temperature on the stability of some complexes was one of the issues of interest. Depending on current national projects and scenarios, the temperature of interest for the deep geological disposal of nuclear waste ranges from 0 °C – deep permafrost penetration – to more than 100 °C – accidental scenarios –. Within this range, effects of temperature are not always negligible, thus there was a need of values for the formation enthalpies, entropies, and heat capacities of some species, which were not always available in the literature. Therefore, the effect of temperature was investigated for the complexation between hexavalent uranium and sulphate on the one hand, and between tetravalent thorium and phosphate on the other hand.

The topics of the work were: i) the analyses of previous data on americium and curium carbonates $Am(CO_3)_n^{3-2n}$ and $Cm(CO_3)_n^{3-2n}$ (Vercouter, 2004; 2005a), ii) europium carbonates $Eu(CO_3)_n^{3-2n}$ (Vercouter, 2004; Vercouter *et al.*, 2005c), iii) dedicated experiments on thorium phosphates $Th(H_2PO_4)_n^{4-2n}$ (Ekberg *et al.*, 2010), iv) dedicated experiments on uranium(VI) sulphates $UO_2(SO_4)_n^{2-2n}$ (Vercouter *et al.*, 2008), and analysis of previous trivalent lanthanide sulphates $Ln(SO_4)_n^{3-2n}$ (Vercouter *et al.*, 2005b), v) dedicated experiments on trivalent actinides and europium silicates (Vercouter *et al.*, 2009a; 2009c).

We will present and discuss hereafter an overview of these works.

2. Data provided through FUNMIG

2.1. The carbonate system

The complexation of radionuclides by carbonate has been issue of study in a huge amount of works in the literature. Testimony of these efforts are the publications previously mentioned of the NEA-TDB reviews, as well as the many specific experimental works, which have been mainly conducted at room temperature. Nevertheless, not so many of these experiments were performed at temperatures above 20-25 °C, although higher temperatures can help stabilizing solid phases, which is a prerequisite when performing solubility measurements (Giffaut, 1994). In a large number of examples solubility data were used to propose different stoichiometries of the aqueous complexes in equilibrium with the solid phases, and to obtain their stability values. Because the speciation may involve a number of species and due to the scattering of solubility measurements that is usually not negligible, the interpretation model of the data is often not unique, and has to be carefully tested. For instance, a very long discussion in the open literature was maintained during the last decades, *e.g.*, on the stability of the thorium carbonate complexes. A consensus seems to have been reached in Rand *et al.* (2009).

The use of solubility experiments to establish stoichiometry and stability of aqueous complexes may present some limitations that cannot be solved if complementary analytical techniques are not used. Some of the limitations associated to solubility experiments result from the very low solubility of most actinides solid phases under geological conditions – especially for An(III) and An(IV) –. In addition, actinide and lanthanide solid phases exhibit a tendency to form colloidal particles (Altmaier *et al.*, 2004; Wang *et al.*, 2006) in the metastability domain around the solubility limits (see Figure 7.2 in Stumm and Morgan, 1996). This requires the use of adequate techniques for particle detection (Walther, 2003),

and often complicates the validation of solubility data interpretation models with equilibrium reactions.

A second limitation of solubility experiments is that in many cases the characterization of the solubility-controlling solid phase is ambiguous and even the solid phases suffer of transformations during the experiment that preclude a reliable understanding of the processes occurring in the set up – the accessible parameter is in fact the product of the solubility product K_s and the complexation constant β_n –. Consequently, the univocal determination of the aqueous complexes in equilibrium with the solid phase(s), which is based upon slope analyses of solubility curves, requires testing different models with different sets of equilibriums. This may lead to a too large amount of unknown parameters as to elucidate the stoichiometry of the species existing in the system.

The solubility analyses of actinide and lanthanide carbonate phases is a good illustration of these issues. As stated in NEA reviews (Silva *et al.*, 1995) "Am(III) solubility studies in carbonate solutions are associated with ambiguities and uncertainties arising from possible solid phase transformations and/or alterations". Most of the solubility data used in deriving NEA selected thermodynamic parameters on americium carbonate phases had been obtain under ambient conditions (20 ≤ T °C ≤ 25, Table 12-8, p369-370 in Guillaumont *et al.*, 2003), and higher temperature were not considered. Increasing temperature usually favours a better crystallisation of the solids and probably reduces the scattering of the solubility measurements. Solubility measurements of solid americium carbonate phases had been performed at different temperatures between 10 and 70°C (Giffaut, 1994). Whereas the NEA expert panel did not considered these data because of the lack of unambiguous solid phase characterisation, these data have been used to determine thermodynamic data of chemical reactions involving Am(III) at 25°C and also for their temperature dependence (Vercouter, 2004; Vercouter *et al.*, 2005a).

Hereafter we report the main information and conclusions, and the new thermodynamic values that have been determined in Vercouter (2004) and Vercouter *et al.* (2005a) from the reinterpretation of the batch experiments at different temperatures in 4 mol/L NaCl in Giffaut (1994). First, the bicarbonate and carbonate concentrations in the batch solutions were corrected for the possible modification of the CO_2(g) partial pressure in equilibrium with the solutions by contact with air during the experiments that lasted several weeks. Because of the lack of XRD analyses, the nature of the solubility-controlling phase can only be determined from the shape of the solubility curves described by the data points. Consequently, different interpretations were tested, based on the nature of the solubility-controlling solid phase and its possible changes during the experiments in order to explain the observed variation of Am(III) solubility at each temperature. The temperature of the batch solutions was varied step by step from 70°C down to 20°C (phase 1), and then up to 70°C again (phase 2). The data at 30 and 70 °C illustrate the results obtained during the two phases of the temperature change (Figure 4).

The Am(III) concentrations measured in phase 1 and phase 2 describe similar solubility curves, which supports that equilibrium was achieved, and that the solid phases had not significantly been altered by the temperature cycle, except maybe for measurements at $[CO_3^{2-}] > 0.1$ mol/L at 70 °C comparing the results from the phase 1 and 2 (Figure 4b). Two main interpretation models were considered: i) a control of the solubility either by $Am_2(CO_3)_3$(s) or $NaAm(CO_3)_2$(s) depending on the carbonate content; ii) a control of the solubility by $AmOHCO_3$(s). According to the representation of data shown in Figure 4 a control of solubility by $Am_2(CO_3)_3$(s) and $NaAm(CO_3)_2$(s) cannot be ruled out compared to the former interpretation of a control by $AmOHCO_3$(s) (Vercouter, 2004; in Supp. Info. of Vercouter *et al.*, 2005a). From this alternative interpretation, another set of thermodynamic parameters have been proposed for both complexation and dissolution reactions. The $AmCO_3^+$, $Am(CO_3)_2^-$, and

$Am(CO_3)_3^{3-}$ stoichiometries have been confirmed as in the original works, but their stepwise formation constants, enthalpy, and entropy were significantly different.

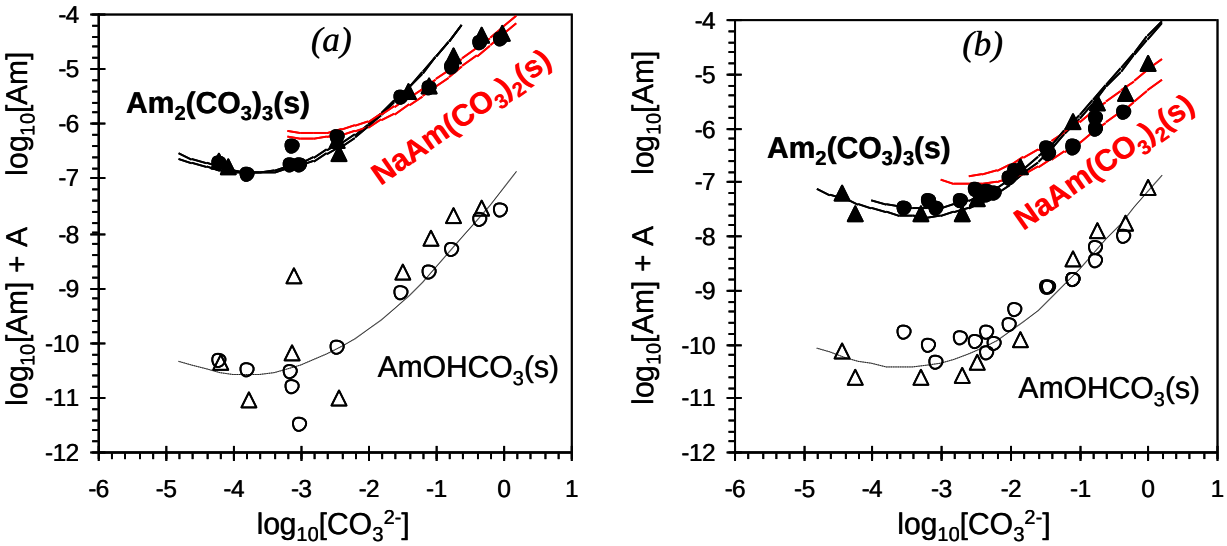

Figure 4. Solubility of Am(III), [Am], in bicarbonate and carbonate solutions with 4 mol/L NaCl measured (□) in phase 1 (cooling) and (□) in phase 2 (heating) for (a) *T = 30°C and* (b) *T = 70°C. The slope analysis suggests that (—) $Am_2(CO_3)_3(s)$ and (—) $NaAm(CO_3)_2(s)$ control the solubility. In the case $AmOHCO_3(s)$ would control the solubility, log[Am] + A is represented (open symbols, dashed line is a guide to the eye), where $A = -0.5 \log_{10}P_{CO_2} + 0.5 \log(K_w^2K_{p2})$, $\log_{10}K_w = -14.17$ (K_w is the ionic product of water at the considered ionic strength) and $\log_{10}K_{p2} = 17.70$ (K_{p2} is the equilibrium constant for $CO_3^{2-} + 2\,H^+ \rightleftarrows CO_2(g) + H_2O$) (Reprinted with permission from Vercouter* et al.*, 2005a. Copyright 2005 American Chemical Society).*

A good agreement is obtained with the Cm(III) data in Table 1 measured by TRLFS at high Na^+ total concentration between 10°C and 70 °C (Vercouter *et al.*, 2005a). From the TRLFS spectra, only one contribution was evidenced for $-1.0 \leq \log_{10}[CO_3^{2-}] \leq 0.3$, and the modification of spectrum was only occurring for lower $[CO_3^{2-}]$ values. The stepwise constant proposed for equilibrium

$$Cm(CO_3)_2^- + CO_3^{2-} \rightleftarrows Cm(CO_3)_3^{3-}$$

was $\log_{10}K_3$(3 mol/L) = 2.01 ± 0.05, with an extrapolation to zero ionic strength using the specific interaction theory (SIT, Grenthe *et al.*, 1992) of $\log_{10}K°_3$ = 0.9 ± 0.1. This value is similar to $\log_{10}K°_3$ = 0.9 ± 0.2 obtained for Am(III) from the re-interpreted solubility data in 4 mol/L NaCl (Table 1). Hence, the value of the cumulative constant for the equilibrium

$$Cm^{3+} + 3CO_3^{2-} \rightleftarrows Cm(CO_3)_3^{3-}$$

is proposed to be $\log_{10}\beta°_3$ = 13.84 ± 0.64 instead of 15 ± 1 selected in Guillaumont *et al.* (2003).

Table 1. Thermodynamic data at 25 °C extrapolated to I *= 0, and for 4 mol/L NaCl (Am) (Giffaut, 1994) reinterpreted in (Vercouter* et al.*, 2005a), and for 3 mol/L $NaClO_4$ (Cm) (Vercouter* et al.*, 2005a).*

Equilibrium	$\log_{10}K°$	$\log_{10}K$	Δ_rG kJ/mol	Δ_rH kJ/mol	Δ_rC_p J/mol/K	Δ_rS J/mol/K
		I = 4 mol/L NaCl				
$AmCO_3^+ + CO_3^{2-} \rightleftarrows Am(CO_3)_2^-$	4.4±0.2 (*) 4.2±0.3 (**) 4.5±0.4 (+) 4.9±0.5 (++)	3.8±0.1	-21.5±0.6	-5.7±12.1	-1340±560	53±29
$Am(CO_3)_2^- + CO_3^{2-} \rightleftarrows Am(CO_3)_3^{3-}$	0.9±0.2 (*) 1.2±0.3 (**) 2.9±0.5 (+) 2.1±0.8 (++)	2.0±0.1	-11.5±0.6	10±10		72±23
		I = 3 mol/L $NaClO_4$				
$Cm(CO_3)_2^- + CO_3^{2-} \rightleftarrows Cm(CO_3)_3^{3-}$	0.9±0.1 (*)	2.01±0.05	-11.5±0.3	12.2±4.4		79±16

(*) Extrapolation to zero ionic strength of $\log_{10}K$(25°C) values derived from data at different temperatures, using SIT parameter from Silva *et al.* (1995).
(**) Extrapolation to zero ionic strength using the values obtained in 3 mol/L $NaClO_4$, 0.1 mol/L and 4 mol/L NaCl at 22±2°C (Vercouter, 2004).
(+) Silva *et al.* (1995) (++) Guillaumont *et al.* (2003)

Stepwise formation constants derived from americium (III) solubility data have been fitted with the SIT formula (Table 1). The $\log_{10}K_2°$ values are in fairly good agreement with the values determined from solubility studies at ambient temperature (Vercouter, 2004), as well as with values selected in NEA-TDB reviews (Table 1). However, the $\log_{10}K_3°$ value differs significantly from the NEA selection. The possible reasons of such discrepancy are discussed

in more details in Vercouter *et al.* (2005a). In particular, Guillaumont *et al.* (2003) selected $Am(CO_3)_3^{3-}$ as the highest carbonato complex of Am(III), but they also discussed values from TRLFS experiments on Cm(III) interpreted with $Cm(CO_3)_4^{5-}$ as the limiting complex (Fanghänel *et al.*, 1998; 1999). Solubility data on Am(III) and Eu(III), analysed with straight lines whose slopes are related to the stoichiometries of the aqueous complexes at equilibrium, support the stability of tricarbonato complexes as limiting complexes (Vercouter, 2004; Vercouter *et al.*, 2005a; Vercouter *et al.*, 2005c). For instance, the slope analysis of the solubility curves of Am(III) measured at different temperatures does not evidence the presence of $Am(CO_3)_4^{5-}$ (Figure 4), in agreement with the NEA review panel's statement for Am(III). The same conclusion was made for Eu(III) for which only maximum possible values of $\log_{10}K_4$ could be determined (Vercouter *et al.*, 2005c).

A repartition of Am(III) species using the present value of $\log_{10}K_3°$ is shown in Figure 5. It appears clearly that under this hypothesis the tricarbonato americium (III) complex exists in a more restricted domain than predicted with the NEA selected values (see Figure 3b).

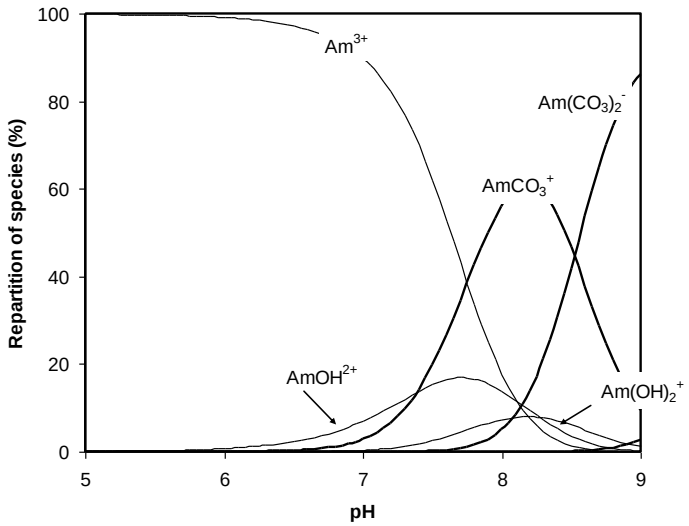

Figure 5. Repartition of species for trace concentration of Am(III) considering I *= 1 mol/L, and* $pCO_2 = 10^{-3.46}$ *atm, with the selected values of Guillaumont* et al. *(2003), except* $\log_{10}K°_3 = 0.9$ *for the stepwise formation of* $Am(CO_3)_3^{3-}$ *from Vercouter* et al. *(2005a).*

Consequently, TRLFS data on Cm(III) have been interpreted considering an analogous behaviour, on the contrary to what was proposed by Fanghänel *et al.* (1998; 1999). Conflicting interpretations of TRLFS data for Cm(III) between Fanghänel *et al.* (1998; 1999) and Vercouter *et al.* (2005a), may come from differences in the fitting hypotheses, *i.e.* stoichiometries of complexes, or from additional effects related to the high ionic strength of the solution, which induces variations of activity coefficients, especially for highly charged complexes. This discrepancies may be resolved by focusing on the aqueous complexes that would be stable in concentrated carbonate solutions, by examining relevant studies on Am(III), Cm(III), and Ln(III). The stability of the limiting carbonate complexes $M(CO_3)_3^{3-}$ or $M(CO_3)_4^{5-}$, in the f-block series for lanthanides and actinides is a question of debate, and both stoichiometries have been considered in experimental studies. Some authors proposed the formation of (Eu or Cm)$(CO_3)_4^{3-}$, which are more or less in the middle of the f-series, from solubility studies (Faucherre *et al.*, 1966), from spectroscopic observations (Fanghänel *et al.*, 1998), or from solvent extraction interpretation (Rao and Chatt, 1991).

Vercouter *et al.* (2005c) studied the equilibrium

$$NaEu(CO_3)_2{\cdot}5H_2O(s) + (n\text{-}2)\ CO_3^{2-} \rightleftarrows Eu(CO_3)_n^{3-2n} + Na^+ + 5H_2O$$

by solubility experiments in $NaClO_4$ and NaCl, and by TRLFS. The latter techniques indicated that only one carbonate complex was present at $[Na^+]_{total}$ = 3 mol/L, and that only dissociation of this complex occurs when decreasing $[Na^+]$ and $[CO_3^{2-}]$. From the Eu(III) fluorescence decay time analysis, the number of remaining water molecules in the first hydration sphere (about 2) seemed to be consistent with the formation of $Eu(CO_3)_3^{3-}$, but the inherent uncertainty of this analysis (± 0.5 Kimura *et al.*, 1996) did not permit to fully ascertain the stoichiometry. The solubility curve determined as a function of the CO_3^{2-} concentration was

actually a straight line in the molar concentration range $-2 \leq \log_{10}[CO_3^{2-}] \leq 0$, whose slope was consistent with n = 3, that is with a dominance of $Eu(CO_3)_3^{3-}$ in solution.

According to previous solubility measurements of $KEu(CO_3)_2 \cdot 5H_2O(s)$, the complex $Eu(CO_3)_4^{5-}$ was apparently stable in the molar concentration range $-2 \leq \log_{10}[CO_3^{2-}] \leq 0$ and in K^+ media, supposedly through the stabilization of the highly charged complex by ion-pairing (Faucherre *et al.*, 1966). However, a more likely explanation would be that the solid-solution system did not reach the equilibrium after the 24 h contacting time, leading to an apparent slope of the solubility curve (Vercouter *et al.*, 2005c; Philippini *et al.*, 2008). Interestingly, other solubility measurements for Ce(III) support the stoichiometry $Ce(CO_3)_4^{5-}$ in concentrated carbonate solutions (Ferri *et al.*, 1983). Recently, Philippini *et al.* (2008; 2010) investigated the stability of limiting carbonate complexes of Ln(III) by solubility method and TRLFS (Philippini *et al.*, 2010) and by capillary electrophoresis hyphenated to ICP-MS (Philippini *et al.*, 2008), and confirmed that both $Ln(CO_3)_3^{3-}$ and $Ln(CO_3)_4^{5-}$ could be stable: The tetra-carbonato complex could only be significantly formed with sufficiently big Ln^{3+} ions, *i.e.* in the beginning of the lanthanide series, in agreement with the solubility results on Ce(III) (Ferri *et al.*, 1983).

Through these studies, it appears that the stoichiometry of the limiting carbonate complexes mainly depends on the size of the metal ion as observed along the Ln(III) series, which suggest to be cautious with the use of analogies in these particular cases: For Am(III) and Cm(III), the limiting complex would be a tricarbonato complex by analogy with Eu(III) and a tetracarbonato complex by analogy to Nd(III). The difference in the stabilisation energy between the two stoichiometries is weak, and close to experimental or data interpretation uncertainties.

2.2. The phosphate system

The review of the panel of experts of the OECD NEA-TDB project in charge of thorium thermodynamic data (Rand *et al.*, 2009) was finally issued after the end of the FUNMIG project. In the aforementioned review, a thorough revision of the available experimental data on the complexation between Th(IV) and phosphate is presented. The authors comment on the different data available in the literature, obtained either by liquid-liquid extraction or by solubility measurements. As already mentioned, solubility experiments present important drawbacks related to the ambiguous characterization of the solid phase, so that the existing data were not selected as sufficiently reliable by the review panel. A publication is under preparation on the EXAFS characterization of gel formation at higher Th and phosphate concentrations (Ekberg *et al.*, in prep), what also complicates interpretation of experimental data if not considered. Rand *et al.* (2009) comment on the ambiguity of the data presented by Fourest *et al.* (1999), which is one of the few works that present data at circumneutral and alkaline *p*H ranges. Östhols (1995) also measured solubility data, in this case of a presumably well characterized ThO_2(cr), although under the used experimental conditions the authors proposed that the aqueous speciation seemed to be dominated by hydroxo-phosphate complexes and therefore the stability of the phosphate complexes could not be obtained. Östhols (1995) also pointed out that the fit of the experimental data was rather poor and that the ThO_2 surface contained phosphor after the solubility experiment. Although more than 10 experimental studies are reviewed, the review panel selected data from Zebroski *et al.* (1951) as the most extensive research work on the complex formation in the Th(IV)-phosphate system (Rand *et al.*, 2009). The corresponding selection of data from Zebroski *et al.* (1951), performed at important H^+ activity, *i.e.*, $0.25 \leq a_{H^+}$ mol/L ≤ 2 and $I = 0.2$ mol/L $(Na,H)ClO_4$, leads to the stability constants of the different complexes formed between Th^{4+} and H_3PO_4(aq) shown in Table 2.

Table 2. Formation constants for the different Th-phosphate complexes selected in Rand et al. *(2009) and proposed in Ekberg* et al. *(2010).*

Equilibrium	$\log_{10}\beta°$
	Rand *et al.* (2009)
$Th^{4+} + H_3PO_4 \rightleftarrows ThH_3PO_4^{4+}$	1.89 ± 0.31
$Th^{4+} + H_3PO_4 \rightleftarrows ThH_2PO_4^{3+} + H^+$	3.45 ± 0.32
$Th^{4+} + 2H_3PO_4 \rightleftarrows Th(H_2PO_4)_2^{2+} + 2H^+$	6.20 ± 0.32
$Th^{4+} + 2H_3PO_4 \rightleftarrows Th(H_3PO_4)(H_2PO_4)^{3+} + H^+$	5.42 ± 0.32
	Ekberg *et al.* (2010)
$Th^{4+} + HPO_4^{2-} \rightleftarrows ThHPO_4^{2+}$	$\log_{10}\beta_1$ (1 M) ≈ 9 $\log_{10}\beta°_1$ ≈ 12 (extrapolated*)
$Th^{4+} + 2HPO_4^{2-} \rightleftarrows Th(HPO_4)_2(aq)$	$\log_{10}\beta_1$ (1 M) =17±3.5 $\log_{10}\beta°_2$ = 21.5±3.5 (extrapolated*)
$Th^{4+} + 3HPO_4^{2-} \rightleftarrows Th(HPO_4)_3^{2-}$	$\log_{10}\beta_1$ (1 M) = 23.7 ± 0.2 $\log_{10}\beta°_3$ = 28.3 ± 0.3 (extrapolated*)

* Extrapolation to zero ionic strength of $\log_{10}\beta$(1 M) values using the ion specific interaction coefficients values in Rand *et al.* (2009) for $\varepsilon(Na^+,HPO_4^{2-})$ = -0.15 ± 0.06, and $\varepsilon(Th^{4+},ClO_4^-)$ = 0.7 ± 0.1. The values of $\varepsilon(ThHPO_4^{2+}, ClO_4^-)$ = 0.4 ± 0.1 kg/mol is taken from $\varepsilon(Th(H_2PO_4)_2^{2+}, ClO_4^-)$ in Rand *et al.* (2009), and $\varepsilon(Na^+, Th(HPO_4)_3^{2-})$ = -0.1 ± 0.2 kg/mol from $\varepsilon(Na^+, Th(OH)_2(CO_3)_2^{2-})$ and $\varepsilon(Na^+, Th(OH)_4CO_3^{2-})$ in Rand *et al.* (2009), respectively. Auxiliary data on phosphate hydrolysis are from Rand *et al.* (2009).

This speciation scheme leads to the aqueous distribution of species shown in Figure 6a, using the SIT, for total phosphate concentration of 10^{-4} mol PO_4/L, from where it can be seen that selected phosphate species dominate at acidic *p*H values but are negligible at *p*H ≥ 4.5, given that only species with the di- or the tri-hydrogenphosphate have been postulated to exist. This fact leaves an open gap when trying to calculate the impact that the complexation of Th(IV) by phosphates can have in the *p*H range of interest for geological disposal of nuclear waste, which can extend up to the hyperalkaline range.

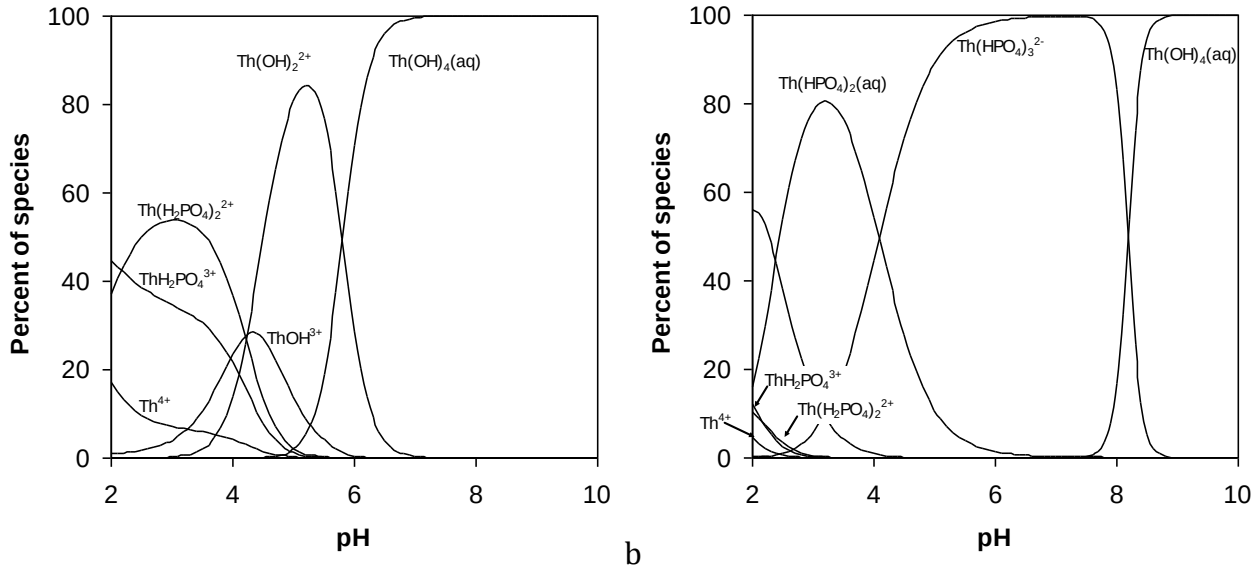

Figure 6 Solution speciation of the thorium phosphate system at I *= 0.1 mol/L (NaClO$_4$), [PO$_4$]$_{tot}$ = 10^{-4} mol/L from the data selected in Rand* et al. *(2009) (a, left), and including data from Ekberg* et al. *(2010) in Table 2 (b, right).*

Within the project, Ekberg *et al.* (2010) performed experimental determinations of the complexation of Th(IV) by phosphates in the *p*H range 7 to 9. The experimental technique used was liquid-liquid extraction.

In many cases, studies of extraction and distribution between two immiscible liquids are performed by batch techniques. After separation, samples are taken in each individual phase and analyzed for their metal content. This method can induce important difficulties to the process in case of multisampling and for this reason Ekberg *et al*. (2010) used the AKUFVE technique. This technique consists on having two phases (usually an aqueous solution and an organic solution) in equilibrium with each other while each phase at the same time is continuously available for on-line analysis (Rydberg, 1969). From the analyses, it was concluded that the phosphate species participating in the complexation with Th(IV) was HPO_4^{2-} at *p*H 8 under the experimental conditions. Therefore this result complements the thermodynamic data selected by Rand *et al*. (2009) and provides parameters needed to calculate the speciation of Th(IV) and phosphate at circumneutral *p*H values.

Ekberg *et al.* (2010) evaluated the stability constants of the 1:1, 1:2 and 1:3 complexes formed in 1 mol/L (Na,H)ClO_4 at 15, 25 and 35 °C and at *p*H 7, 8 and 8.7 with enthalpy and entropy determined with the obtained stability constants for the 1:2 and 1:3 complexes.

The stability constants obtained by these authors at 1 mol/L (Na,H)ClO_4 ionic strength, extrapolated to infinite dilution by the SIT are shown in Table 2. The first constant $\log_{10}\beta°_1$ is only an approximation as the experimental set-up did not permit to obtain low enough competing ligand concentration. Therefore, this constant was rather determined by extrapolation of $\log_{10}\beta_3$ and $\log_{10}\beta_2$.

Extrapolation using SIT to $\log_{10}\beta°$ has been done with the specific interaction coefficient selected in Rand *et al.* (2009) for H^+, Th^{4+}, and HPO_4^{2-}, *i.e.* $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ kg/mol, $\varepsilon(Th^{4+}, ClO_4^-) = 0.7 \pm 0.1$ kg/mol, $\varepsilon(Na^+, HPO_4^{2-}) = -0.15 \pm 0.06$ kg/mol. The values of specific ion interaction coefficient are estimated *via* analogy to be $\varepsilon(ThHPO_4^{2+}, ClO_4^-) = 0.4 \pm 0.1$ kg/mol – from $Th(H_2PO_4)_2^{2+}$ in Rand *et al.* (2009) –, and $\varepsilon(Na^+, Th(HPO_4)_3^{2-}) = -0.1 \pm 0.2$ kg/mol – from $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4CO_3^{2-}$ in Rand *et al.* (2009), also in agreement with $\varepsilon(Na^+, Th(SO_4)_3^{2-}) = -0.091 \pm 0.038$ –, respectively.

The resulting speciation is shown in Figure 6b, using the SIT, as function of *p*H at 0.1 mol/L ($NaClO_4$) and $[PO_4]_{total} = 10^{-4}$ mol/L. Under these conditions, the phosphate complexes proposed by Ekberg *et al.* (2010) would dominate over the hydroxo complexes of Th(IV) in a larger *p*H range.

It can be seen that the speciation changes completely. The adequacy or reliability of the constants obtained by Ekberg *et al.* (2010) cannot be tested in front of analogue elements data given that no data for tetravalent actinide aqueous phosphate are available in the literature under circumneutral *p*H conditions, as pointed out by Rand *et al.* (2009). The importance of $ThHPO_4^{2+}$ can also be questioned as its $\log_{10}\beta°_1$ value is only estimation.

2.3. The sulphate system

2.3.1. Uranium(VI)-Sulphate

Vercouter *et al.* (2008) studied the uranium(VI) sulphate system. They used TRLFS to record the spectra of several solutions containing U(VI)-sulphate complexes. From the analyses of the solutions at 0.1 mol/L Na^+ ionic medium at 25 °C, stability constants of the two first sulphato complexes of U(VI) were determined and found to be close to the data selected by Guillaumont *et al.* (2003) (see Table 3).

The temperature dependence of the reactions was determined from the results of the fluorescence spectra at 6 different temperatures in the interval 10-75 °C. No dependence on the enthalpy of reaction with temperature was assumed, so that $\Delta_r C_p = 0$. the formation of UO_2SO_4(aq) was found to be even more endothermic by about 10 kJ/mol compared with the data selected in Guillaumont *et al.* (2003). The formation enthalpy for $UO_2(SO_4)_2^{2-}$ was found to be similar (Table 3).

Table 3. Formation constants for the uranium(VI)-sulphate complexes

Equilibrium	Thermodynamic data and constants
$UO_2^{2+} + SO_4^{2-} \rightleftarrows UO_2SO_4$(aq)	Grenthe *et al.* (1992) $\log_{10}K° = 3.15 \pm 0.02$ $\Delta_r H°_m$ (kJ/mol) = 19.5 ± 1.6 Vercouter *et al.* (2008) $\log_{10}K° = 3.29 \pm 0.10$ $\Delta_r H°_m$ (kJ/mol) = 29.1 ± 4.0
UO_2SO_4(aq) + $SO_4^{2-} \rightleftarrows UO_2(SO_4)_2^{2-}$	Grenthe *et al.* (1992) $\log_{10}K° = 0.99 \pm 0.07$ $\Delta_r H°_m$ (kJ/mol) = 15.6 ± 1.3 Vercouter *et al.* (2008) $\log_{10}K° = 1.04 \pm 0.10$ $\Delta_r H°_m$ (kJ/mol) =16.6 ± 4.5

A review of the calorimetric data in the literature showed that discrepancies do exist, especially for the first complexation reaction (Vercouter *et al.*, 2009b). The $\Delta_r H$ for the

monosulphato complex formation proposed in Vercouter *et al.* (2008) was however in good agreement with the calorimetric determination by Bailey and Larson (1971) after reinterpretation with the $\log_{10}\beta°_1$ recommended value in Guillaumont *et al.* (2003). Recently, Tian and Rao (2009) carried out calorimetric and spectroscopic measurements at I = 1.0 mol/L that resulted in additional values: $\Delta_r H_m^{cal}$ = 17.7 ± 0.3 and $\Delta_r H_m^{spec}$ = 16.1 ± 1.7 kJ/mol for the formation of UO_2SO_4(aq), and $\Delta_r H_m^{cal}$ = 25.5 ± 0.8 and $\Delta_r H_m^{spec}$ = 26.9 ± 1.2 kJ/mol for the stepwise formation of $UO_2(SO_4)_2^{2-}$. Significant differences with the previous sets can also be noticed (Table 3), which probably emphasizes the difficulty of getting accurate values for the formation of such moderate complexes. The $\Delta_r H°_m$ of the stepwise reactions of sulphate complexation are positive, indicating that the reactions are endothermic and that the main contribution to the enthalpy is the dehydration energy.

Vercouter *et al.* (2008) evidenced the formation of the trisulphato uranyl(VI) complex at high sulphate concentration in 3 mol/L Na^+ ionic medium. Under these conditions, only pieces of evidence of the third complex were found, while the spectroscopic signatures of the other two complexes could not be clearly obtained. A value of the stepwise constant in 3 mol/L Na^+ medium was determined for the following equilibrium.

$UO_2(SO_4)_2^{2-} + SO_4^{2-} \rightleftarrows UO_2(SO_4)_3^{4-}$ $\log_{10}K_3 = 0.76 \pm 0.20$

The extrapolated $\log_{10}\beta_3°$ was not proposed, because the corresponding SIT parameters are unknown and can be hardly estimated. The authors judged that the extrapolation would incorporate more errors in the calculated magnitude than the analytical error itself.

The value selected by Guillaumont *et al.* (2003) for the reaction

$UO_2^{2+} + 3SO_4^{2-} \rightleftarrows UO_2(SO_4)_3^{4-}$ $\log_{10}\beta_3° = 3.02 \pm 0.38$

was adopted from the work of Geipel *et al.* (1996) as it was the only data available in the literature. The extrapolation to infinite dilution with SIT was made in Guillaumont *et al.*

(2003) by estimating the interaction coefficient $\varepsilon(Na^+,UO_2(SO_4)_3^{4-})$ from $\varepsilon(Na^+, UO_2(CO_3)_3^{4-})$, *i.e.* - (0.01 ± 0.11) kg/mol. With the same parameters, $\log_{10}\beta_3° = 3.09$ is obtained from the constants at I = 3 mol/L (Vercouter *et al.*, 2008). Although it looks consistent with the NEA selected value, it is not obvious that the simple SIT equation can be applied to a concentrated sulphate medium (Ciavatta *et al.*, 2003).

The enthalpy of the reaction for the stepwise constant of the third complex was determined in Vercouter *et al.* (2008). A value of $\Delta_r H°_m$ = 11 ± 8 kJ/mol was obtained, showing that the coordination of uranyl by a third sulphate ligand is less endothermic than the coordination by the second sulphate, which is in turn less endothermic than the coordination by the first sulphate ligand. This is a usual trend for actinide complex formation with inorganic anions. The enthalpy values suggest the possibility of sulphate anions acting as monodentate and bidentate ligands towards UO_2^{2+} in the third complex, as it happens in the case of the uranyl acetate (Vercouter *et al.*, 2008).

2.3.2. Lanthanide/Actinide-Sulphate system

The complexation of lanthanides (III) by sulphate anions

$$Ln^{3+} + nSO_4^{2-} \rightleftarrows Ln(SO_4)_n^{3-2n}$$

was also studied in the framework of a clayey interstitial water (Vercouter *et al.*, 2005b).

Similarly to the carbonate system, differences in Am(III) sulphate selected data in a former NEA review (Silva *et al.*, 1995) and its update (Guillaumont *et al.*, 2003). In Guillaumont *et al.* (2003), it is estimated that ion-exchange and solvent extraction data, which formed the basis of the former selection, are probing different phenomena as compared to spectroscopic techniques, due to the existence of both outer- and inner-sphere complexes. This argument can be questioned and was discussed in depth in Vercouter *et al.* (2005b). Nevertheless, the

update review has preferentially used spectroscopic data on Cm(III) in NaCl (Paviet *et al.*, 1996; Neck *et al.*, 1998) for monosulphato and disulphato complexes of americium(III).

The sulphate complexation of the analogous Eu(III) was therefore investigated by TRLFS at $I \leq 2.2$ mol/kg (Na_2SO_4, $NaClO_4$), and the sulphate complexation of La(III) was also checked by nano-electrospray ionization mass spectroscopy at low ionic strength (HNO_3, H_2SO_4). Since the TRLFS analysis provided a more complete set of results, only these data are reported here.

The authors tested different modelling of their data, and concluded that the best fit was obtained when considering two inner sphere complexes $EuSO_4^+$ and $Eu(SO_4)_2^-$, leading to $\log_{10}\beta°_1 = 3.78 \pm 0.06$ and $\log_{10}K°_2 = 1.5 \pm 0.2$, and hence $\log_{10}\beta°_2 = 5.3 \pm 0.2$. These values compare well with other experimental values for Eu(III) and also with the Am(III) data selected in Silva *et al.* (1995), *i.e.*, $\log_{10}\beta°_1 = 3.85 \pm 0.03$ and $\log_{10}\beta°_2 = 5.4 \pm 0.7$, suggesting that the analogy between Eu(III) and Am(III) is relevant. These data predict a higher stability of the complexes compared with that predicted with the selected data in Guillaumont *et al.* (2003) based on $\log_{10}\beta°_1 = 3.30 \pm 0.15$ and $\log_{10}\beta°_2 = 3.70 \pm 0.15$. These differences can be seen in Figure 7a,b at varying sulphate concentration in acidic medium (I = 3 mol/L), using the SIT. The differences are mainly due to the stability of the disulphato americium(III) complex. In a water composition more representative of an argillaceous water (Gaucher *et al.*, 2009), the differences in $AmSO_4^+$ concentrations can be viewed in Figure 7c,d where the proportion in monosulphato americium (III) complex is halved between the former review (Silva *et al.*, 1995) and the latter (Guillaumont *et al.*, 2003). The data obtained within FUNMIG tends to be in favour of the former selection, which supports the analogy between Eu(III) and Am(III). The analogy between Am(III) with Cm(III) was already apparent in Silva *et al.* (1995) from ion-exchange and solvent extraction studies, and it should also be noted that these values of complexation constants are also very similar to what was selected for Pu(III) (Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

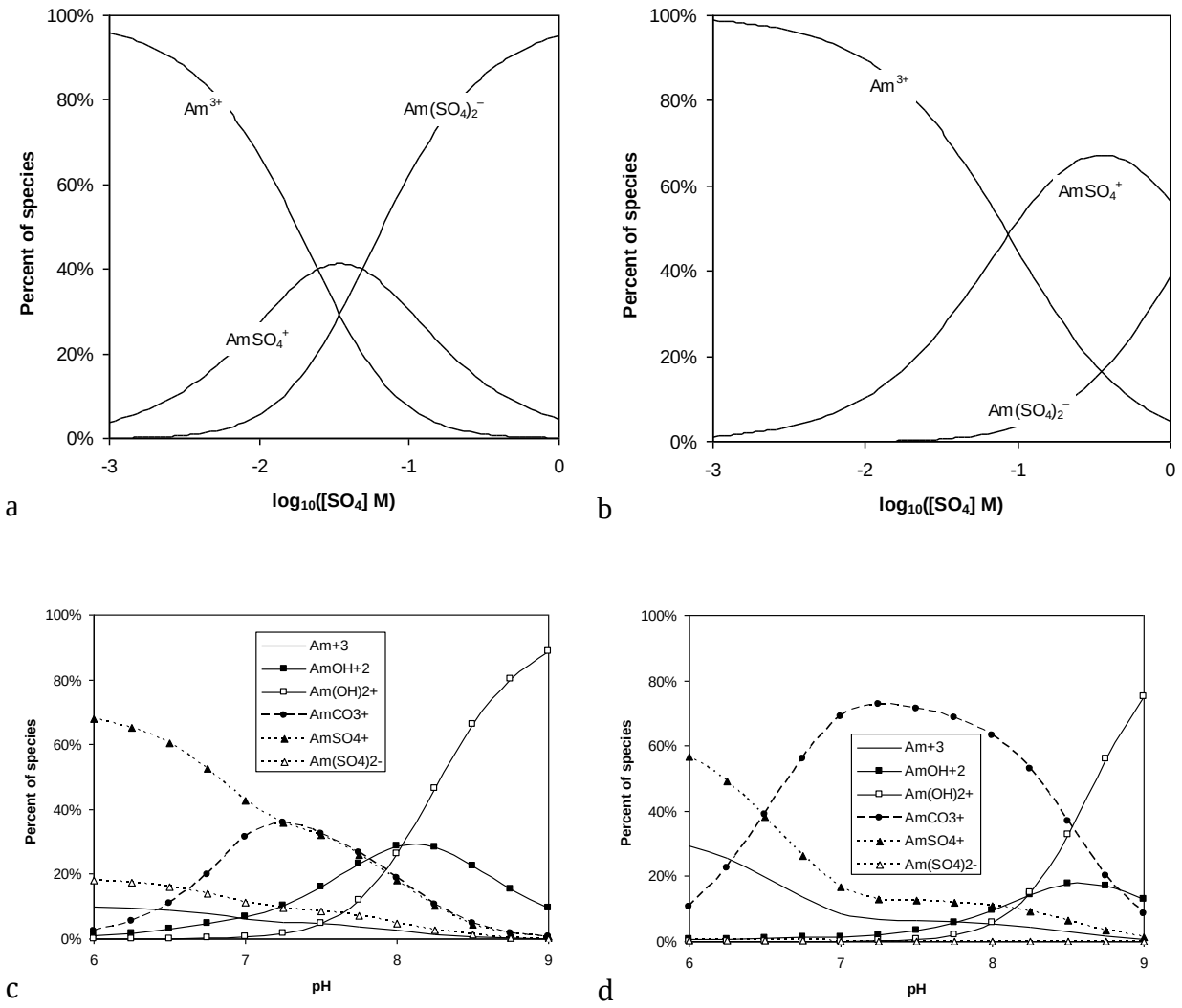

Figure 7. Differences in the repartition of Am(III) species using $Am(SO_4)_n^{3-2n}$ constants from (a, c, left) Silva et al. *(1995), and (b, d, right) Guillaumont* et al. *(2003) varying total sulphate concentration, for* I *= 3 mol/L (a, b, up), and varying* p*H in equilibrium with $(Ca,Mg)(CO_3)_2/CaCO_3$ at $[S]_{total}$ = 39 mmol/L (Gaucher* et al.*, 2009) (c, d, down).*

2.4. The silicate system

The silicate system was studied within the FUNMIG project in order to settle difficulties of retention experiments interpretation in clay media. One of the outcomes of this work was a review of the literature data (Vercouter *et al.*, 2009c) where some of the main inconsistencies and gaps were identified. Among others, the authors remarked the difficulty in studying the

system in a way that the polymerization of silicic acid is avoided. Most experimental data in the literature has been obtained at acidic *p*H values, where the observation of the complexes results easier, although it becomes evident that the polymerization of silicic acid occurs even in acidic solutions for concentrations of Si above 2 10^{-3} mol/L. In any case, pieces of evidence for the formation of monosilicic complexes of Am(III), Cm(III) and Eu(III) occur, although polymerization of silicates could explain the discrepancies in the published stability constants of more than one order of magnitude. The selected data in Guillaumont *et al.* (2003) is $\log_{10}K°$ = -1.68 ± 0.18 for the following reaction

$$Am^{3+} + Si(OH)_4 \rightleftarrows AmOSi(OH)_3^{2+} + H^+$$

The interaction of lanthanides and trivalent actinides with silicates can be of interest in different aspects of the evaluation of the migration of these elements. An illustration of the relative relevance of carbonate versus silicate complexes of Am(III), referring to Guillaumont *et al.* (2003), is shown in Figure 8a, using Phreeplot (Kinniburgh and Copper, 2009) and embedded PHREEQC. The dominant aqueous species of Am(III) are represented as a function of silicate and carbonate concentrations at *p*H 7. It is clear from this representation that either $AmCO_3^+$ or $AmOSi(OH)_3^{2+}$ dominates the speciation depending on the carbonate and silicate content of the water. Using Phreeplot and PHREEQC, in Figure 8b it is assumed that the solution is equilibrated either with quartz or with Mg-Montmorillonite-Na using solubility product from Guillaumont *et al.* (2003) and Blanc and Gailhanou (2007), respectively. It implies that the concentration of Si in solution ranges from 10^{-5} to 10^{-4} M. The concentration range is coherent with actual values in clays (Degueldre *et al.*, 2003; de Craen *et al.*, 2004; Gaucher *et al.*, 2006; Beaucaire *et al.*, 2008). In this case, the parameters A = $[Si(OH)_4(aq)]/[HCO_3^-]$ and B = $[Si(OH)_4(aq)].[H^+]$ control the predominance of one or the other species. They are to be compared to the following equilibrium constants calculated from Guillaumont *et al.* (2003).

$AmOSi(OH)_3^{2+} + HCO_3^- \rightleftarrows AmCO_3^+ + Si(OH)_4(aq)$ $\log_{10}K° = 0.85$

$AmOSi(OH)_3^{2+} + 2H_2O \rightleftarrows Am(OH)_2^+ + Si(OH)_4(aq) + H^+$ $\log_{10}K° = -13.42$

At the considered ionic strength, for A or B values higher than $K[AmOSi(OH)_3^{2+}/AmCO_3^+]$ and $K[AmOSi(OH)_3^{2+}/Am(OH)_2^+]$, respectively, the silicate species dominates. For A or B values lower than the K values, the carbonato or hydroxo species dominate. Noteworthy is the fact that using the $\log_{10}K°[Cm^{3+}/Cm(CO_3)_3^{3-}]$ proposed by Vercouter *et al.* (2005a) would draw the $Am(CO_3)_2^-/Am(CO_3)_3^{3-}$ border out of the limit of Figure 8b.

From the previous Figures it seems clear that the complexation of Am(III), and analogous trivalent elements, with silicate may influence the mobility and interactions in, for example, the vicinity of the clay buffer material installed in the repository to buffer water intrusion.

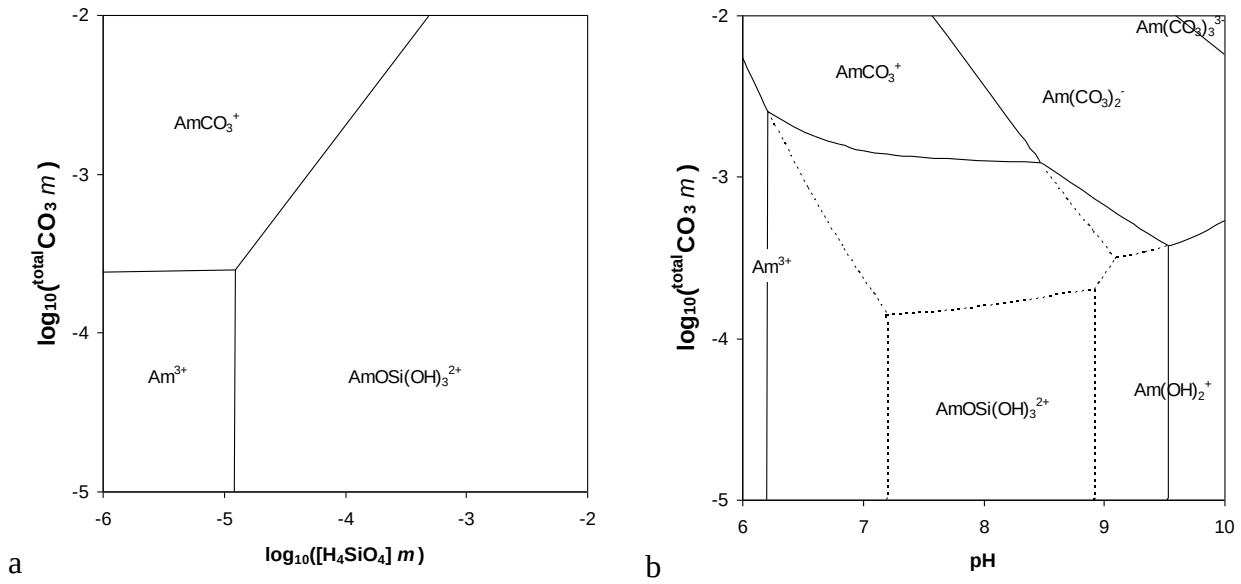

Figure 8. Predominance diagram of americium(III) aqueous species from Guillaumont et al. *(2003) in the carbonate-silicate domain at* p*H 7 (a, left) and in the carbonate-*p*H domain (b, right) for waters equilibrated with quartz (plain line, Guillaumont* et al.*, 2003), and Mg-Montmorillonite-Na (dotted line, Blanc and Gailhanou, 2007), at* I *= 0.1 mol/L* $NaClO_4$*.* $Am(CO_3)_n^{2-n}$*.*

One of the advances made during the experimental program of the project was the use of novel techniques to establish structure and elucidate different structural rearrangements in solution. One example of this advance is the use of electrospray ionisation mass spectrometry (ESI-MS). ESI-MS is based on a soft ionization process that keeps ions largely intact, and generates a mass spectrum from which species can be identified by the mass-to-charge ratio of the parent complex ion. This technique has recently succeeded in detecting silicate oligomeric species formed in aqueous solutions containing structure-directing templates for the synthesis of zeolites or mesoporous structures (Bussian *et al.*, 2000; Eggers *et al.*, 2005; Pelster *et al.*, 2007).

Vercouter *et al.* (2009a) studied the complexation of Eu(III) with orthosilicic acid by TRLFS in acidic conditions. Although the solutions were undersaturated with respect to amorphous silica, where monomeric $Si(OH)_4$ is expected to be the only Si species, the data could not be interpreted only considering the $EuOSi(OH)_3^{2+}$ complex, and suggested the presence of polymeric or colloidal particles interacting with the Eu^{3+} ions. These observations were similar to the ones reported in the case of Cm(III) solutions in similar conditions (Panak *et al.*, 2005). The negative mode of ESI-MS was used to check the presence of oligomeric silicates in the solutions. The ionization process was considered to be soft enough to limit dehydroxylation reactions during the formation of the spray. Figure 9 shows an ESI mass spectrum of a 10^{-3} mol/L silicate solution at *p*H 5, where the different peaks are attributed to the different fragments indicated in the inserts. A number of oligomeric silicate species were identified, which may be related to their presence in the aqueous solution. When increasing the *p*H of the aqueous solutions, the peak intensities of the monomeric silicates decrease whereas the peak intensities of the oligomeric species increase. Such a trend is also expected in aqueous solutions, which supports that ESI-MS can effectively probe the distribution of silicate species in solution. But, these oligomeric species are not supposed to be prominent

under these conditions, and $H_5Si_2O_7^-$ should only represent 5% at pH 10 at equilibrium with quartz from thermodynamic data (Guillaumont *et al.*, 2003). The actual presence of the oligomeric species in low silicate and slightly acidic media is a question of interest since it may have biased the thermodynamic constants of metal-silicate complexes. Production of new experimental data accounting for oligomers formation is highly recommended. This point is especially relevant given that oligomeric species are usually neglected in speciation modelling of radionuclides in naturally relevant solutions, so that the detection of oligomeric silicate compounds at low concentration is an analytical challenge.

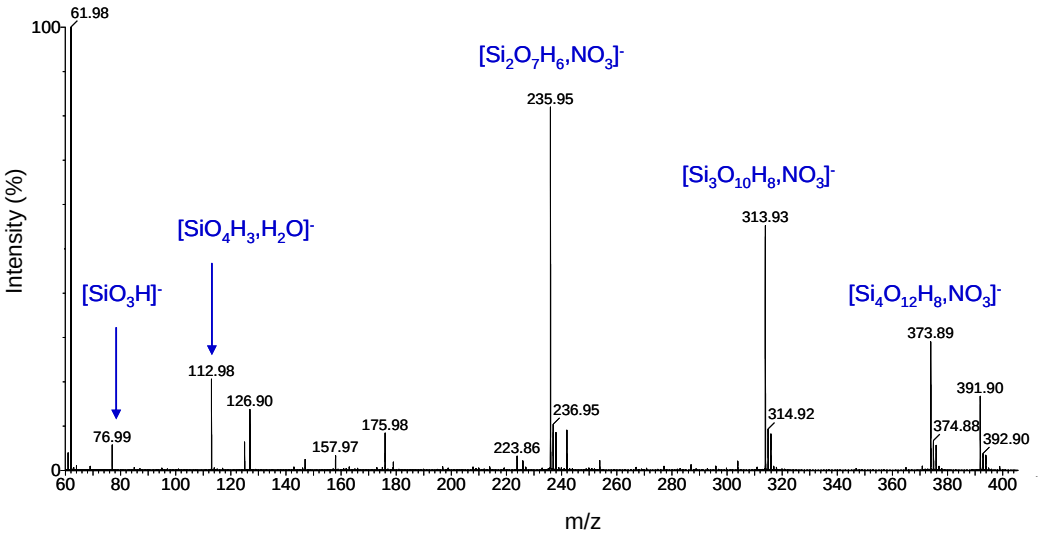

Figure 9. ESI mass spectrum of a 10^{-3} mol/L silicate solution at pH *5 (Vercouter* et al.*, 2009a)*.

In their review of the stability of trivalent actinides silicate complexes and lanthanides, Vercouter *et al.* (2009c) compared the formation constants measured for Eu(III) (Jensen and Choppin, 1996; Pathak and Choppin, 2006; Thakur *et al.*, 2007), Am(III) (Wadsak *et al.*, 2000; Thakur *et al.*, 2007) and Cm(III) (Steinle *et al.*, 1997; Panak *et al.*, 2005; Pathak and Choppin, 2006; Thakur *et al.*, 2007) to assess possible discrepancies of the data existing in the literature (see Figure 10). The authors remarked that the values recommended in Guillaumont *et al.* (2003) for the stability constants of Am(III) and Cm(III) agreed with only some experimental values. The experimental value for Cm(III) in Panak *et al.* (2005) is lower than the one

predicted, and the values obtained by Thakur *et al.* (2007) for Eu, Cm, and Am are significantly higher than the ones obtained by following the recommendation in Guillaumont *et al.* (2003). The resulting range of possible values for this $\log_{10}\beta°_1$ is thus from -2.2 (adjusting to Panak *et al.*, 2005) to -1.0 (adjusting to Thakur *et al.*, 2007). The NEA selected value appears to be a reasonable mean of these estimations. To account for this distribution, it would then be necessary to increase the $\log_{10}\beta°_1$ uncertainty from 0.18 to at least 0.5.

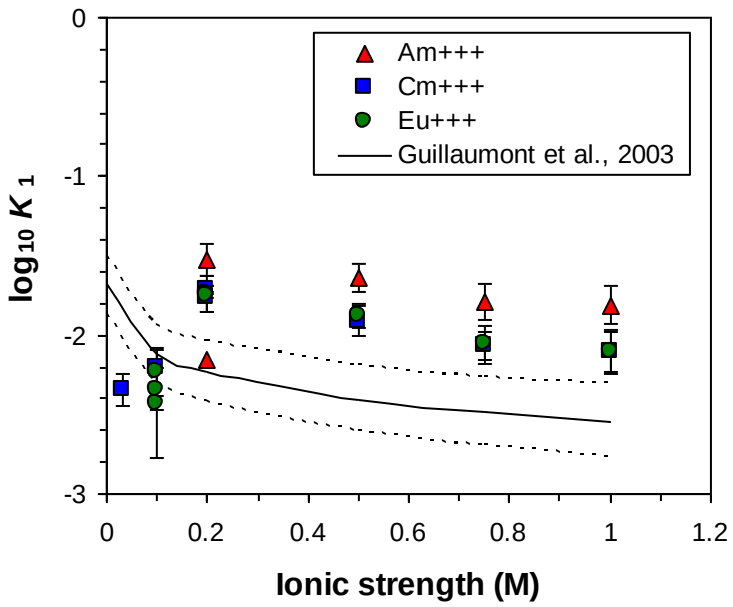

Figure 10. Values of the formation constants of the monosilicate complexes of Am(III) (triangle: Wadsak et al.*, 2000; Thakur* et al.*, 2007), Cm(III) (square: Steinle* et al.*, 1997; Panak* et al.*, 2005; Pathak and Choppin, 2006), and Eu(III) (circle Jensen and Choppin, 1996; Pathak and Choppin, 2006; Thakur* et al.*, 2007) as a function of the experimental ionic strengths. The theoretical curve from Guillaumont* et al. *(2003) is represented with the corresponding uncertainties (dashed line).*

3. Conclusions, perspectives and prospective

The contribution of FUNMIG to deepen in the knowledge of thermodynamic properties of radionuclides was focused on the complexation of lanthanides and actinides by carbonate,

sulphate, phosphate, and silicate. Some of the values selected in NEA-TDB reviews have been confirmed while others are proposed to be modified. These new values can be used to calculate the aqueous speciation of actinides under conditions relevant for the long-term storage of radioactive wastes.

Americium was one of the actinides whose thermodynamic data was more extensively studied within the project. In Figure 11 the predominance diagram, of the americium species at *p*H 7 and total sulphate concentration between 14 and 40 mM is obtained using Phreeplot. These values are representing the lowest value for which $AmSO_4^+$ is prominant over Am^{3+}, and the solubility limit in clay environment (Gaucher *et al.*, 2009). Sulphate concentration can be significantly lower, *e.g.* between 0.01 up to 20 mM (Degueldre *et al.*, 2003; Beaucaire *et al.*, 2008). It can be seen that, depending on the total silicate concentration, the situation varies. At *p*H 7, $-2 \leq \log_{10}[^{total}CO_3] \leq -3$ and $-5 \leq \log_{10}[Si(OH)_4(aq)] \leq -4$, *i.e.* in equilibrium with a clayey environment, and I = 0.1 mol/L, the coexistence of at least three different mono-complexes is predicted. If the silicate concentration is controlled by SiO_2(am), *i.e.*, $\log_{10}[Si(OH)_4(aq)] = -2.7$ (Gunnarsson and Arnorsson, 2000), then the americium speciation should even be more controlled by the silicate system. In addition, it seems that oligomeric silicates may be present in rather acidic media, as observed in the framework of the project by ESI-MS. These oligomeric silicates seem to influence the speciation of actinides(III) (Panak *et al.*, 2005).

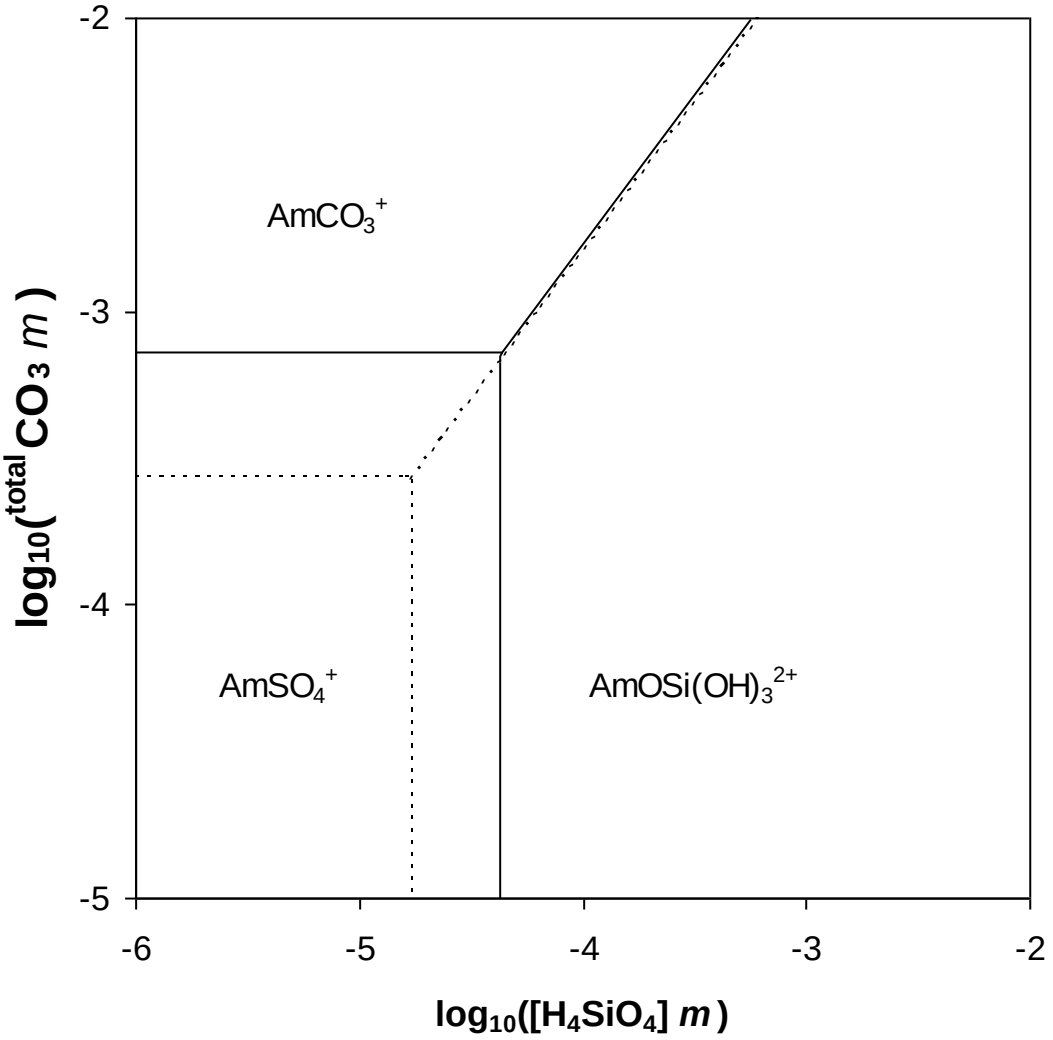

Figure 11. Predominance diagram of traces of americium(III) at p*H 7, total sulphate concentration between 14 mM (dotted) and 40 mM (plain), 0.1 mol* $NaClO_4$ */L, and varying* $[Si(OH)_4(aq)]$ *and total carbonate. Thermodynamic data from Guillaumont* et al. *(2003), except for* $Am(SO_4)_n^{3-2n}$ *from Silva* et al. *(1995).*

Only the carbonate, sulphate, and silicate complexes are considered in this exercise. Other inorganic complexes, as phosphate, or natural or anthropogenic organic complexes potentially affecting the current speciation were not taken into consideration. It is noteworthy that very little information are known for the temperature dependence of the stability of $AmCO_3^+$ and $AmOSi(OH)_3^{2+}$ complexes although they are relevant stoichiometries as shown in Figure 11.

The work in the thorium phosphate system indicates the formation of this type of complexes for *p*H values higher than the ones in the previous literature data, and allows the calculation of the effect of phosphate in the behaviour of thorium in *p*H of interest for nuclear waste management studies. The impact that the formation of these species may have on the solubility of thorium at *p*H 8 and I = 0.1 mol $NaClO_4$/L is shown in Figure 12. It can be seen that a concentration of phosphate higher that 10^{-4} is needed to have a measurable effect confirming the assumption of Östhols (1995). Enthalpies of reaction have also been estimated.

The results obtained from the study of the complexation of uranyl by sulphate at different temperatures permitted the estimation of $\Delta_r H$ of the three $UO_2(SO_4)_n^{2-2n}$ complexes.

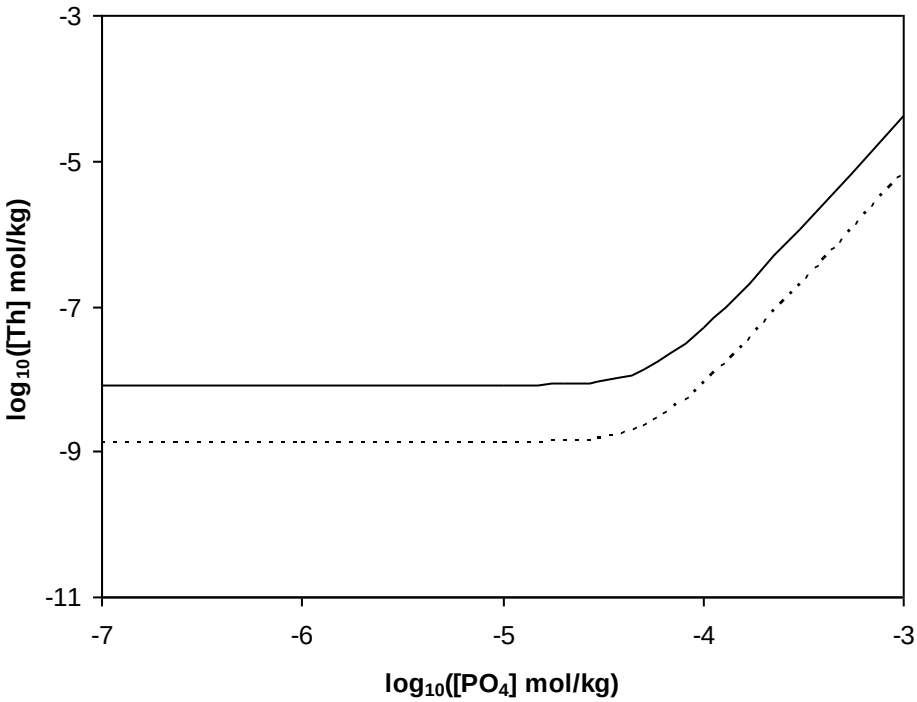

Figure 12. Effect of the $Th(HPO_4)_n^{4-2n}$ *complexes proposed in Ekberg* et al. *(2010), and extrapolated in Table 2 on the solubility at* p*H 8 and* I *= 0.1 mol* $NaClO_4$ */L of* ThO_2*(am,hyd,aged) (dotted) and* ThO_2*(am,hyd,fresh) (plain) from Rand* et al. *(2009).*

In these works, the combination of different techniques, liquid-liquid extraction, solubility measurements, TRLFS, and also ESI-MS, has allowed to complete thermodynamic data bases with experimental determinations. Some promising results have been obtained, in some cases

only preliminary due to the short time of duration of the project, but in any case the outcome of the works conducted in the frame of FUNMIG should contribute to improve models based on thermodynamic data.

4. Acknowledgment.

Special thanks are due to all the partners from RTDC-1 of FUNMIG, as well as to Drs. Catherine Beaucaire and David G. Kinniburgh for helpful discussions, and Drs Wolfgang Hummel and Eric Giffaut for their fruitful comments.

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