ORGANICS

1.1 SELECTION PROCEDURE FOR ORGANIC COMPLEXATION: LOW MOLECULAR WEIGHT ORGANICS

Organic compounds contained in radioactive waste can be classified into different categories. The ability of organic compounds to form stable complexes with metallic cations is widely recognized. The effect of Low Molecular Weight (LMW) organic compounds present in the wastes, or produced via their degradation on the mobilization of radionuclides under repository conditions must be assessed. For this reason, one of the tasks within the ANDRA project is to study the stability of the complexes formed between these ligands and radionuclides.

- *Bitumen from bituminized wastes.* Bitumen is used as an immobilization matrix as it provides both physical and chemical stability (IAEA, 1993). It consists predominantly of carbon (80 to 88% by weight) and hydrogen (8 to 11%), with smaller amounts of oxygen (1 to 12%), sulphur (1 to 7%) and nitrogen (trace to 1.5%) (Walczak, 2000). Oxalate and acetate are some representative bitumen degradation products under alkaline conditions (Kagawa et al., 2000).

- *Cement additives.* Cement additives are used to enhance the physical and rheological properties of concretes, and are essential in the construction of a disposal facility for radioactive waste. They are also used in the waste conditioning and the concrete waste packaging. These organic materials can be classified into different groups, depending on their functional group: Sulphonate-based superplasticizers ($R-SO_3^-$), polycarboxylate derivatives ($R-COO^-/R-OH$) and other superplasticizers (as vynil copolimers). Although they are much stable in alkaline media, they eventually can suffer degradation; in this case, they are expected to degrade into smaller organics compounds with functional groups such as COH, CO, CO_2H or sulphonic acid, amines and carboxylate salts. Simple polyhydroxy carboxylic acids (such as gluconate) have been used in some cases as a surrogate of the polycarboxylate additives (ANDRA, 2005b, Bradbury & Van Loon, 1998). As a matter of fact, gluconate may represent the upper limit effect that a carboxylic ether superplasticizer could have on radionuclide mobilization, thus being a very conservative estimation. On the other hand, polycarboxylates also typically contain a range of minor components to improve the performance of the intended application. Among these minor components, gluconate may be used in order to prevent an excessive rapid sorption of the superplasticizer onto the cement (Hayes et al., 2012).

- *Chemicals used for decontamination and cleaning.* Multidentate chelating agents such as citrate, NTA or EDTA, are widely used in the nuclear industry for the decontamination of reactors and equipment (Ayres, 1971). These compounds are especially versatile because of their ability to form stable, water-soluble complexes with a wide range of metal ions; the strength of a metal complex depends on the denticity of the complexing agent (Means and Alexander, 1981).

- *Polymers, filters and resins.* A number of ILW packages contain a variety of organic compounds such as plastics or resins (ANDRA, 2005). Among plastics, it is possible to find a wide variety of materials, as polyvinyl chloride (PVC), polyurethane (PUR), polyethylene (PE)… Ion exchange resins (and similar products such as organic polymers contained in filters) may consist of polystyrene chains with amines as the active groups in anion exchangers and sulphonic or carboxylic acids in cation exchangers (Allard and Persson, 1985; ANDRA, 2005). Furthermore, the mechanical properties of some plastics as PVC can be modified through the addition of low molecular weight compounds (plasticizers) that mix with the polymer matrix. Those additives (adipic and phthalic acids, among others) have been shown to leach into water without degradation of the original macromolecule, increasing the concentration of organics in solution.

- *Cellulose.* Cellulose is a common material in ILW/LLW wastes, due to its presence in everyday materials such as tissues, cloth, paper or filters. It is a polysaccharide with a linear condensation polymeric chain with the formula $(C_6H_{10}O_5)_n$. It consists of glucose units (D-anhydroglucopyranose units) connected through β-1,4-glycosidic bonds and is also known as β-1,4-D-glucan (polyglucose) (Wertz et al., 2010). Alkaline degradation of cellulose under anaerobic conditions yields isosaccharinic acid (ISA), which has been found to have an important impact on the chemistry of radionuclides present in the repository (Hummel et al., 2005; Gaona et al., 2008).

Taking into account those organics present in the wastes and their degradation products, the need of updating the last advances in the selection of stability data was acknowledged. The strategy followed to obtain this information depended on the specific characteristics of the ligand and the amount of data available in the open literature, and is described in the following sections.

The general methodology followed was:

- Evaluation of the influence of organic compounds by considering the stability constants of the complexes formed with metals and radionuclides available in previous compilations (Pearson et al., 1992; Hummel, 1993. This work is reported in Gaona et al. (2006a).

- Extensive bibliographical review based on both the NEA compilation (Hummel et al., 2005) and open literature.

The literature research and review completed has allowed the identification of several gaps especially regarding:

- Stoichiometry and stability of ternary complexes.
- Data missing in the open literature for some of these ligands, specially adipate and phthalate.

A specific experimental task devoted to the study of the gaps identified in the gluconate and isosaccharinate system within the alkaline pH range has been carried out.


1.1.1 Literature review and data selection

The general methodology followed for literature review and data selection was:

- Evaluation of the influence of organic compounds by considering the stability constants of the complexes formed with metals and radionuclides available in previous compilations (Pearson et al., 1992 and Hummel, 1993. This work is reported in Gaona et al. (2006a).
- Extensive bibliographic review based on both the NEA compilation (Hummel et al., 2005) and open literature.

1.1.1.1 Input to Thermochimie: oxalate, citrate and EDTA

The work undertaken for oxalate, citrate and EDTA includes a revision of the acid base properties of these organic ligands, their complexation with Ca and their complexation with the following radionuclides: U, Np, Pu, Am, Tc, Se, Ni and Zr.

Oxalate   Citrate   EDTA[4-]
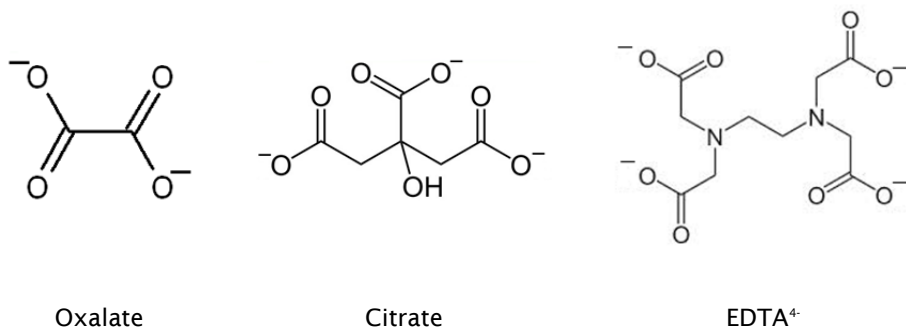
Chemical structures for oxalate, citrate and EDTA[4-].

### 1.1.1.2   Input to Thermochimie: NTA, acetate, adipate and phthalate

The NEA publication (Hummel et al., 2005) does not include data for NTA, acetate, adipate or phthalate. Thus, the thermodynamic data selection for these organic ligands is mainly based on the data available on the open literature. The level of information available varies strongly depending on the organic ligand considered; there is a significant lack of data in the open literature for adipate and phthalate complexes with radionuclides.

NTA[3-]   Acetate   Adipate   Phthalate
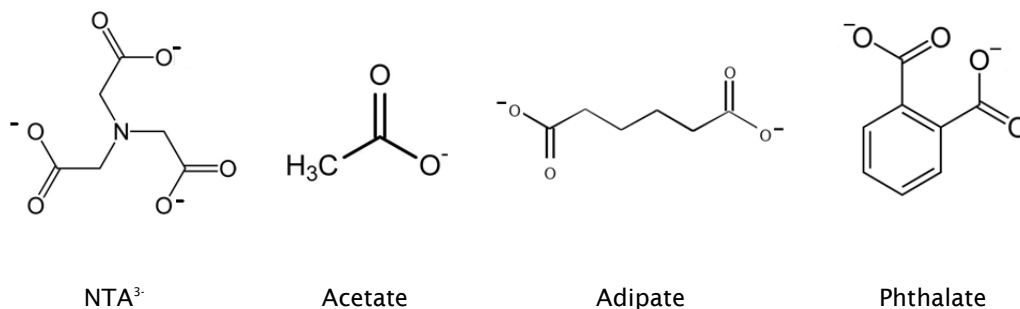
Chemical structures for NTA[3-], acetate, adipate and phthalate.

1.1.1.3   Input to Thermochimie: ISA and gluconate

The preliminary thermodynamic data selection regarding radionuclide complexation with isosaccharinate and gluconate is reported in Gaona et al. (2006c).
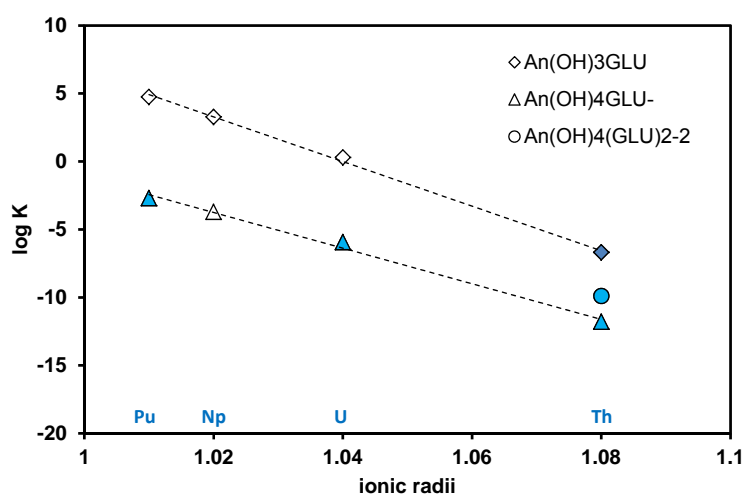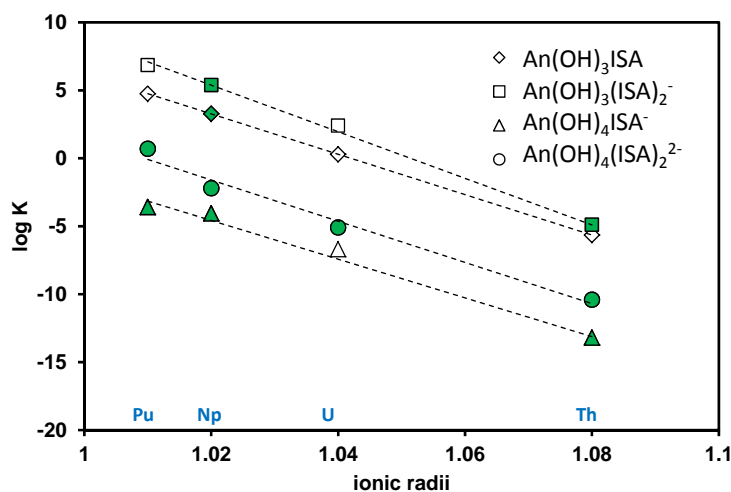

Isosaccharinate   Gluconate
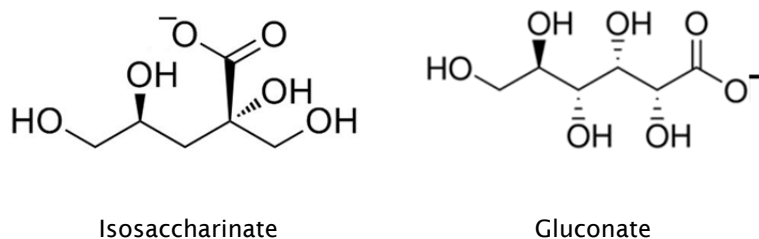
Chemical structures for isosaccharinate and gluconate.

Selection was made according to the following methodology:

- **Literature review and selection of reaction data**.

- **Estimations** based on ionic radii correlations and on analogies between ISA and GLU in case no experimental data were available.

- **Correction of ionic strength**. SIT approach was preferred, although due to the lack of interaction coefficients, Debye-Hückel was applied in most cases.

- **Estimations of uncertainties** taking into account discrepancies amongst the different experimental sources whenever the error associated to a given value was not available.

The available thermodynamic data on An(IV)–ISA/GLU complexes were reviewed and re-calculated to ensure the internal consistency of the stability constants assessed. Estimations based on Linear Free-Energy Relationships (LFER) among tetravalent actinides and analogies between ISA and GLU complexes were performed when needed. An example is provided in the figure below where log K values of isosaccharinate and gluconate complexes for tetravalent radionuclides included in Thermochimie are shown.

Log K values for isosaccharinate (up) and gluconate (down) complexes of tetravalent elements included in ThermoChimie, as a function of the ionic radii of the radionuclide. Filled symbols: data obtained from reevaluation of experimental sources. Open symbols: data obtained through analogies or ionic radii correlations.

This approach led to the selection of some aqueous species of Th, U, Np and Pu with ISA and GLU forming in alkaline to hyperalkaline pH conditions and their corresponding conditional stability constants.

Furthermore, some gaps concerning radionuclides complexation with isosaccharinate and gluconate were identified. These gaps led to the development of a specific experimental program.

The experimental program is focused on the organic ligands forming the strongest complexes, namely gluconate ("GH_4^-"), isosaccharinate ("$ISAH_2^-$") and EDTA ("$EDTA^{4-}$"). Thorium and uranium have been selected as representative of a major group of safety-relevant radionuclides present in the waste matrix. Results have been obtained mainly from two different types of experiments: macroscopic solubility experiments (from both undersaturation and oversaturation directions) and spectroscopic analyses (EXAFS and UV-VIS).

The specific objectives was fourfold:

1- To obtain reliable thermodynamic data (stability constants) of the thorium-gluconate system;

2- To fill in the gaps of experimental data in both gluconate and isosaccharinate system, and to compare the data obtained in order to check if gluconate is a good analogue for isosaccharinate chemical behaviour;

3- To study the role of calcium in the thorium-gluconate and thorium-EDTA systems;

4- And to study the U(VI)-gluconate and U(VI)-EDTA systems.

This work has led to the publication of several scientific papers (Colàs et al. 2011, 2012, 2013a, 2013b) and several presentations in workshops and conferences.

The correlation between the stability constants and the Gibbs free energy of An(IV) (linear free-energy relationship) were used to assess the reliability of stability constants along the An(IV) series (Choppin et al., 2006; Gaona et al., 2008; Meyer et al., 2007; Rojo et al., 2013). The results of the correlation are shown in the figure below; the stability constant of the thorium-gluconate complex obtained in the frame of this experimental program (1:1 complex, equation rewritten in terms of Th^{4+}) is shown in red. As seen in the figure, the result shows a good agreement with other data available in the literature for An(IV)-gluconate complexes.
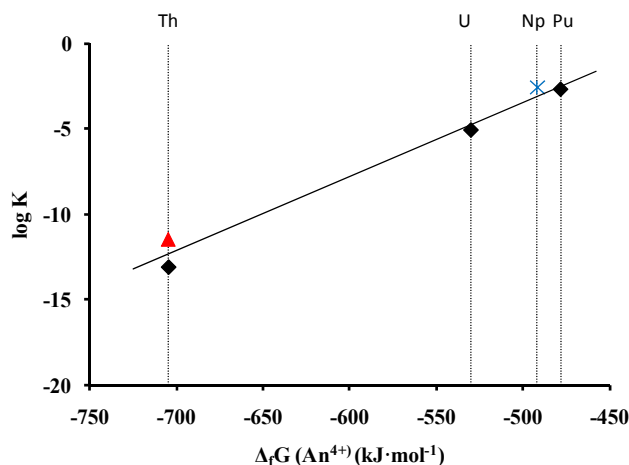
Relationship between the stability constants of An(IV)-gluconate complexes with $\Delta_f G(An^{4+})$, adapted from (Rojo et al. 2013). Red triangle stands for thorium-gluconate stability constant obtained in present work. Blue cross: from (Rojo et al. 2013). Black symbols: values recalculated from (Cross et al. 1989, Felmy 2004, Moreton 1993, Warwick et al. 2004).

1.1.1.4 Th(IV)-isosaccharinate system in the alkaline range

Stability constants for the formation of 1:1 and 1:2 Th-isosaccharinate complexes were also determined using solubility experiments. The value obtained for the 1:2 thorium-isosaccharinate complex was only approximate, due to the differences observed in the experiments from oversaturation or undersaturation direction. The stability constants for thorium-isosaccharinate complexes obtained in present work agree with previous solubility experiments (Rai et al., 2009) and with liquid-liquid extraction measurements (Allard and Ekberg, 2006a; 2006b) from the literature. However, the constants are lower than the values previously determined in sorption experiments (Vercammen, 2000; Vercammen et al., 1999; 2001).

Although gluconate is usually used as a chemical analogue for isosaccharinate, small differences were obtained in solubility experiments in the presence of gluconate or isosaccharinate. This suggests that this analogy should be used with caution, being gluconate effect on thorium hydroxide solubility higher than that of isosaccharinate.

1.1.1.5 Effect of calcium

The presence of competing ions should then be taken into account when calculating the influence of the organic ligands on radionuclide mobility. The case of calcium is particularly significant, assuming that this element is one of the main components of cement (an ubiquitous material in the radioactive waste repositories).

The formation of ternary Ca-Th-L species (where L is a polyhydroxycarboxylic acid) had been reported in some publications (Tits et al. 2005, Vercammen et al. 1999). Considering that, thorium hydroxide solubility experiments in the presence of both gluconate and calcium were carried out over the alkaline pH range in order to investigate the formation of these complexes. Only at higher calcium concentrations, $[Ca]=2.2 \cdot 10^{-2}$ M, a small increase in solubility (in comparison with the data in absence of calcium) is observed. In the same sense, EXAFS studies did not allow to observe any changes in the structure of the thorium-gluconate complex when calcium was present in the media. Thus, the formation of ternary Ca-Th-gluconate species was not confirmed in present work. It was concluded that, in alkaline systems (pH=12) where gluconate is present, calcium concentrations below 10^{-2}M may not enhance significantly thorium hydroxide solubility.

On the other hand, in the Th-EDTA system, calcium was shown to be a significant competitor for thorium, due to the formation of Ca-EDTA complexes. Thus, the presence of calcium reduces thorium mobility in the presence of EDTA. The EDTA structure is significantly different from that of gluconate or isosaccharinate, as it does not contain alcoholic hydroxy groups. With increasing pH, the hydrolysis of the metal ion may prevent the coordination of the EDTA ligand to thorium. For the same reason, thorium complexation with EDTA is significantly affected by the competitive formation of $NaEDTA^{3-}$ and $Ca(EDTA)^{2-}$ complexes, as Na or Ca are less acidic than Th.

1.1.1.6 U(VI)-gluconate and U(VI)-EDTA system in the alkaline range

U(VI)–gluconate and U(VI)-EDTA complexes in the alkaline pH range were investigated. In the case of U(VI)-gluconate system, both solubility and UV-VIS experiments were carried out. The formation of $UO_2(OH)_n(GH_3)^{n-}$ increases significantly sodium and potassium uranates solubility at pH=12 and at gluconate concentrations higher than 10^{-2} M, thus affecting the mobility of U(VI). However, the stoichiometry of this complex remains unclear; further studies are necessary before those conclusions can be extrapolated to other pH values.

U(VI) is predominantly penta coordinated, with all exchangeable ligands perpendicular to the O=U=O axis (Glaus et al., 2000). On the contrary Th(IV) is expected to have a coordination number of 9 or 10 (Szabo et al., 2006) and has a higher tendency to hydrolysis. As a consequence, the complexation of U(VI) with a polyhydroxycarboxylic acid such as gluconate may be weaker than the complexation of Th(IV) with the same ligand.

EDTA concentrations in the range -4 < log [EDTA] < -2.5 do not increase the solubility of sodium uranate at pH=11.8; the experimental data obtained do not allow to deny neither confirm the existence of U(VI)-OH-EDTA species. The geometry of UO_2^{2+} and that of EDTA only permits coordination of one iminodiacetate moiety at most. Consequently, the relative stability of U(VI)-EDTA complexes is expected to be lower than the stability of EDTA complexes with other cations (Glaus et al., 2000), e.g. Th(IV).

1.1.2   Up-dated systems since 2006

The studied systems on the Low Molecular Weight organic compounds present in the wastes, or produced via their degradation, are summarized in the table below. The table reviews the data up-dated since 2006 (included).

The literature research and review done allowed the identification of several gaps especially regarding:

- the stoichiometry and stability of ternary complexes,

- the lack of data in the open literature for some of these ligands, specially adipate and phthalate.

Summary of low molecular weight organic ligands systems updated since 2006.

	Acetic	Adipic	Citric	EDTA	GLU	ISA	NTA	Oxalic	Phthalic
acid/base	✓	✓	✓	✓	✓	✓	✓	✓	✓
Ca	✓	✓	✓	✓	✓	✓	✓	✓	✓
Mg			✓	✓			✓	✓	
Pu	✓			✓	✓	✓	✓	✓	✓
U	✓		✓	✓	✓	✓	✓	✓	✓
Np	✓		✓	✓	✓	✓	✓	✓	
Th	✓		✓	✓	✓	✓	✓		
Eu	✓					✓		✓	✓
Am	✓		✓	✓	✓	✓	✓	✓	✓
Cm								✓	✓
Ni	✓		✓	✓		✓	✓	✓	✓
Tc	✓			✓			✓	✓	

1.2 SELECTION PROCEDURE FOR ORGANIC COMPLEXATION: NATURAL ORGANIC SYSTEM (CALLOVO-OXFORDIAN)

In the context of nuclear waste disposal, kerogen may be subject either to a mild increase of maturation, which may result in a significant generation of CO_2 (Lorant et al., 2008), or to an interaction with an alkaline solution originating from the percolation of water through concrete. The latter interaction results in the degradation of kerogen to produce soluble high molecular weight compounds whose structures resemble those of fulvic and humic acids (Claret et al., 2004). Depending on the prevailing conditions, these soluble compounds may dissociate into low-molecular-weight (LMW) compounds (C_1-C_6 carboxylic acids, phenols...), do react or form complexes with radionuclides, which may in turn be transported in the environment surrounding the repository.

During the development of ThermoChimie regarding radionuclide data, including complexation with simple organic ligands, one of the aims was the review and selection of thermodynamic data on some organic compounds previously selected: benzene, toluene, phenol, o-cresol, benzoic acid and acetic acid (Gaona et al., 2007). The review included a thorough revision of formation data for all compounds, as well as acid-base reaction data for phenol, o-cresol, benzoic acid and acetic acid. The followed strategy consisted of the review of both solubility (solid to water and organic liquid to water) and gas/water partitioning studies. The resulting thermodynamic data selection was used to determine thermodynamic data on key fragments of organic molecules in order to assess the thermodynamic properties of kerogen and fulvic acid materials.

1.2.1 Theoretical models applied to fulvic compounds

Fulvic acids are constituted by a supramolecular assemblage of relatively low-molecular-weight (a few hundreds of Dalton) compounds (LMW) and which are held together in some kind of micellar structure (Sutton and Sposito, 2005). The available thermodynamic properties of the LMW organic compounds have been discussed and critically evaluated in a number of publications (Shock and Helgeson, 1990; Shock, 1995; Amend and Helgeson, 1997). Recent advances in analytical techniques have identified single fulvic acid molecules and propose structures for these molecules (Stenson et al., 2003) and thus to generate idealized molecular models for these fulvic acid- fulvate-like compounds (FAL). This kind of information constitutes the basis for the rationale adopted in the present study for establishing fulvic acid models and calculating their thermodynamic properties using group additivity algorithms.
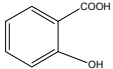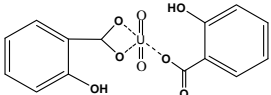
The thermodynamic properties of the molecular groups are first derived from data reported in the literature for simple (LMW) compounds (benzene, toluene, phenol, benzoic acid, etc.). These group properties are subsequently combined in the fulvic acid model structure to estimate the thermodynamic properties of this fulvic acid model. In order to enlarge this approach to the complexation of radionuclides by fulvate-like compounds (FAL), thermodynamic properties of RN-LMW can be directly used in this group additivity scheme to estimate equilibrium constants for the complexation reactions between FAL anions and radionuclides. These estimations can then be compared to experimental equilibrium constants independently determined for natural and synthetic fulvate anions.

The approach has also been extended to study the fixation of iodine by organic matter. Similar to the previous exercise, the methodology followed in the thermodynamic data selection focused on the availability of experimental both solubility and gas/water partitioning data. The scarcity of the thermodynamic data available, though, led this process to be complemented by the thermodynamic data selection conducted for pure liquid and gas organic iodine compounds.
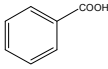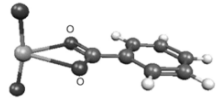
An overview of preliminary information available in the literature for the considered organic-radionuclide complexes, as well as the experimental and thermodynamic approaches is gathered in the tables below.
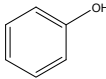
Preliminary information from literature review for salicylic acid complexes.

	Main conclusions	Main gaps	Suggested structures
U(VI)	Stability constants for $[UO_2(C_6H_4COO(O))]$, $[UO_2(C_6H_4COO(O))_2]^{-2}$, $[UO_2(C_6H_4COO(OH))]^+$, $[UO_2(C_6H_4COO(O))OH]^-$ complexes recalculated from Gonçalves and Mota (1987).	Lack of information for complexes formed at pH>7.	Structure for 1U:2L complexes suggested in Denecke et al. (1998) (based on EXFAS data).
Eu(III)	Preliminary stability constants for $[EuC_6H_4(COO)(OH)]^{2+}$ complex recalculated from Aoyagi et al. (2004).	Lack of information for complexes formed at pH>4.	-
Th(IV)	Preliminary stability constant for $[ThC_6H_4(COO)(O)]_2^+$ recalculated from Skorik and Artish (1985).	Lack of information.	-

Preliminary information from literature review for benzoic acid complexes.

	Main conclusions	Main gaps	Suggested structures
U(VI)	Stability constant for $[UO_2(C_6H_5COO)]^+$ complex recalculated from Glorius et al. (2007; 2008); Vulpius, (2005).	Lack of information for complexes formed at pH>4.	Expect structure of the $[UO_2(C_6H_5COO)]^+$ complex reported by Moll et al., 2003; Wiebke et al., 2008 (from EXAFS data).
Eu(III)	Stability constants for $[Eu(C_6H_5(COO)]^{2+}$ and $[Eu(C_6H_5(COO)_2]^+$ complexes recalculated from Wang et al. (1999) and Choppin et al. (1982).	Lack of information for complexes formed at pH>5.	Disagreement about possible structures (Wang et al., 1999; Lam et al., 2003; Vulpius, 2005).
Th(IV)	-	No information available.	-

Preliminary information from literature review for phenol complexes.

	Main conclusions	Main gaps	Suggested structures
U(VI)	Stability constant for $[UO_2(C_6H_5O)]^+$ recalculated from Bartusek & Sommer (1965) and selected only as preliminary.	Lack of information for complexes formed at pH>4.	-
Eu(III)	-	No information available.	-
Th(IV)	Stability constant for $[Th(C_6H_5O)]^{3+}$ recalculated from Óztekin et al. (1996) and selected only as preliminary.	Lack of information.	-

This review has provided the selection of several stability constants that can afterwards be used in the thermodynamic modelling of fulvate-like compounds (FAL). However, most of these data have been obtained at pH<5; there is a lack of complexation data under neutral and alkaline pH conditions.