Nicole Adam*, Katja Hinz, Xavier Gaona*, Petra J. Panak and Marcus Altmaier

Impact of selected cement additives and model compounds on the solubility of Nd(III), Th(IV) and U(VI): screening experiments in alkaline NaCl, $MgCl_2$ and $CaCl_2$ solutions at elevated ionic strength

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Abstract: The solubility of Nd(III), Th(IV) and U(VI) was studied from undersaturation conditions in the presence of selected organic cement additives and model compounds: adipic acid, methyl acrylate, citric acid, melamine, ethylene glycol, phthalic acid and gluconic acid. Experiments were performed under Ar atmosphere in NaCl (2.5 and 5.0 M), $MgCl_2$ (1.0 and 3.5 M) and $CaCl_2$ (1.0 and 3.5 M) solutions with $9 \leq pH_m \leq 13$ ($pH_m = -\log[H^+]$). Initial concentrations of organic ligands in solution were set constant in all systems to $[L]_0 = 0.025$ M, except in specific cases (*e.g.* adipic acid, melamine and phthalic acid) where the ligand concentration in the matrix solutions was lower and controlled by solubility. Adipic acid, methyl acrylate, melamine, ethylene glycol and phthalic acid do not impact the solubility of Nd(III), Th(IV) and U(VI) in the investigated NaCl, $MgCl_2$ and $CaCl_2$ systems. Citrate significantly enhances the solubility of Nd(III), Th(IV) and U(VI) in NaCl systems. A similar effect was observed for Th(IV) and U(VI) in the presence of gluconate in NaCl systems. The impact of pH on the stability of the complexes is different for both ligands. Because of the larger number of alcohol groups in the gluconate molecule, this ligand is prone to form more stable complexes under hyperalkaline conditions that likely involve the deprotonation of several alcohol groups. The complexation of gluconate with U(VI) at $pH_m \approx 13$ is however weaker than at $pH_m \approx 9$ due to the competition with the highly hydrolysed moiety prevailing at $pH_m \approx 13$, *i.e.* $UO_2(OH)_4^{2-}$. The impact of citrate and gluconate in $MgCl_2$ and $CaCl_2$ systems is generally weaker than in NaCl systems, expectedly due to the competition with binary Mg-L and Ca-L complexes. However, the possible formation of ternary complexes further enhancing the solubility is hinted for the systems Mg/Ca-Th(IV)-GLU and Ca-U(VI)-GLU. These observations reflect again the differences in the complexation properties of citrate and gluconate, the key role of the alcohol groups present in the latter ligand, and the importances of interacting matrix cations. The screening experiments conducted within this study contribute to the identification of organic cement additives and model compounds potentially impacting the solution chemistry of An(III)/Ln(III), An(IV) and An(VI) under intermediate to high ionic strength conditions ($2.5 \leq I \leq 10.5$ M). This shows evident differences with respect to investigations conducted in dilute systems, and thus represents a very relevant input in the safety assessment of repositories for radioactive waste disposal where such elevated ionic strength conditions are expected.

Keywords: citrate; gluconate; neodymium; solubility; thorium; uranium.

***Corresponding authors: Nicole Adam** and **Xavier Gaona**, Karlsruhe Institute of Technology (KIT), Campus North, Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany, E-mail: nicole.adam@kit.edu (N. Adam), xavier.gaona@kit.edu (X. Gaona).
Katja Hinz, Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany
Petra J. Panak, Karlsruhe Institute of Technology (KIT), Campus North, Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany; and Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany
Marcus Altmaier, Karlsruhe Institute of Technology (KIT), Campus North, Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany

1 Introduction

Deep underground repositories are favoured by international consensus for the final disposal of radioactive waste. Three different host-rock formations are usually considered for the construction of such facilities, *i.e.* crystalline (granite), clay and salt-rock [1–6]. In the event of water intrusion into the repository, the composition of the pore

water will largely depend on the host-rock material, with granite and clay environments usually leading to low ionic strength systems and salt-rock formations resulting in brine systems with high concentrations of NaCl and $MgCl_2$ solutions ($5 < I < 15$ M). Intermediate ionic strength conditions ($2 < I < 6$ M) are expected in specific clay formations such as Cretaceous argillites in Northern Germany [7] or sedimentary bedrocks in the Canadian Shield [8], among other examples.

The use of concrete and cementitious materials for construction purposes, as backfill material or for the solidification of waste packages can significantly alter the geochemical boundary conditions in the repository. In dilute systems, the dissolution of portlandite and calcium silicate hydrate phases (C-S-H) buffers the pH and Ca concentrations within 10–13.3 and $\approx 10^{-4}$–0.02 M, respectively [9–11]. The corrosion of cementitious material in the presence of high $MgCl_2$ concentration results in the exchange of Ca by Mg in the cement phases, eventually leading to concentrated $CaCl_2$ solutions with $pH_m \approx 12$ in specific cases [12]. This shift in pH can be of high relevance in $MgCl_2$ systems, in which otherwise the pH_m is buffered at ≈9 by the precipitation of $Mg(OH)_2$ or (above 2 m $MgCl_2$ solutions) Mg-OH-Cl solid phases. The presence of high Ca concentrations in the pore water can importantly alter the solution chemistry of the actinides, as previously demonstrated for An(III), An(IV) and An(V) [13–16].

Various types of chemical admixtures are considered in the formulations of concrete and cement to modify/improve the physicochemical properties of these materials, *e.g.* workability, pumpability, durability, shrinkage properties or the mechanical performance. Among other cement additives, retarders and superplasticizers (SPs) are extensively used and play a relevant role in the cement chemistry. The use of retarders delays the hardening time of the slurry, ensuring an appropriate viscosity and pumpability over a given timeframe. For this purpose, mainly hydroxylic acid salts and saccharide derivatives like sodium gluconate or citrate are used [17–20]. Superplasticizers are an important class of cement additives commonly used in modern concrete mixtures to improve dispersion, hydration and workability properties [21]. The superplasticizers are mainly organic polymers which can be subdivided in four different categories: naphthalene-sulfonate based SPs [22], melamine-sulfonate based SPs (or sulfonated melamine formaldehyde [SMF]) [22–24], lignosulfonate based SPs [22] and polycarboxylate-ether based SPs (PCEs) [17,25–28]. The latter are of particular interest since they are commonly used in current cement formulations and modifications of the side chains connected to the polyethylene backbone give access to a large family of polymers with specific properties.

Under the hyperalkaline conditions eventually developing in cementitious environments, organic materials such as cement additives can undergo chemical transformations (*i.e.* hydrolytic, thermal, radiolytic or microbial degradation, ageing, etc.), and subsequently small organic molecules with different chemical properties may form [29–32]. The organic admixtures or degradation products can be leached from the cement and, depending on their chemical properties and complexation strength, impact the solubility and sorption behaviour of the radionuclides in the nuclear waste repository. Previous studies have shown the influence of organic cement admixtures or potential degradation products on the behaviour and mobility of several radionuclides [33–42]. Especially polyhydroxocarboxylic acids like gluconate are able to form strong complexes with actinides and other hard Lewis acids under the hyperalkaline conditions representative of cementitious systems. However, most of these studies focus on low ionic strength conditions and cannot be directly extrapolated to intermediate or high ionic strength systems such as those expected in specific clay systems or rock-salt formations. Besides the effects caused by ion–ion interactions, elevated concentrations of alkaline and especially earth alkaline cations such as Ca^{2+} or Mg^{2+} may lead to the formation of stable complexes with the organic ligands thus decreasing the free organic ligand concentration in solution. On the other hand, the presence of such divalent cations can also promote the formation of very stable ternary complexes as those previously described for Ca–An–L (L = GLU, Cit) [33, 38, 40].

In this work, the solubility of Nd(III), Th(IV) and U(VI) is studied in the presence of selected organic cement additives or model compounds (Figure 1). The considered actinides and lanthanide analogue represent the most relevant oxidation states expected for the actinides under repository-relevant conditions. Gluconate, citrate, adipate and phthalate are directly used as retarders [17–20] or inhibitors [43], whereas melamine, methyl acrylate and ethylene glycol represent components of several frequently used PCE and SMF superplasticizers [17, 23, 25, 26]. Screening experiments at selected pH values in the alkaline range in NaCl, $CaCl_2$ and $MgCl_2$ solutions of intermediate and high ionic strength are performed. This study aims at quantitatively assessing the impact of representative cement additives and model compounds on the solubility of tri-, tetra- and hexavalent actinides under repository-relevant conditions, especially at elevated ionic strength.

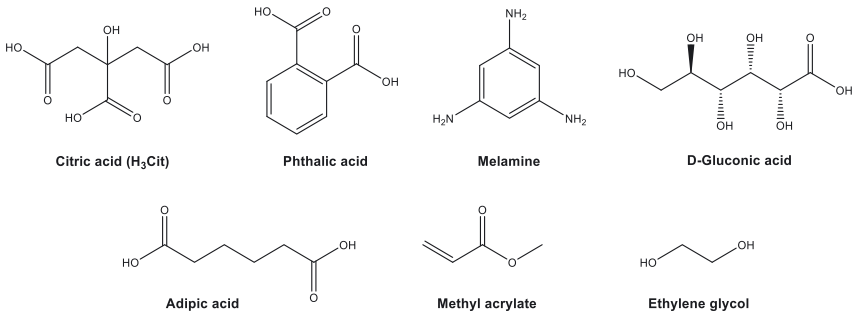


Figure 1: Cement additives and respective model compounds used in the present study.

2 Experimental

2.1 Chemicals

Melamine (≥99%), citric acid (H_3cit, ≥99.5%), ethylene glycol (≥99.8%), phthalic acid (≥99.5%), adipic acid (≥99.5%) and methyl acrylate (≥99%) were obtained from Sigma-Aldrich. NaCl, $CaCl_2$, $MgCl_2$ (p.a.) and sodium gluconate (NaGLU, p.a.) were purchased from Merck. HCl (Titrisol, Merck), NaOH (Titrisol, Merck), $Ca(OH)_2$ (Merck) and $Mg(OH)_2$ (Merck) were used to adjust the pH in NaCl, $CaCl_2$ and $MgCl_2$ systems, respectively. $Th(NO_3)_4{\cdot}5H_2O$ and $UO_2(NO_3)_2{\cdot}6H_2O$ were obtained from Merck. All solutions were prepared using ultrapure water (Millipore, Billerica, MA, USA; 18.2 MΩcm) and purged with Ar for 2 h before use to remove CO_2 in solution. Sample preparation and solubility experiments were performed in a glove box under Ar atmosphere ($O_2 \leq 2$ ppm) at $t = (22 \pm 2)$ °C.

2.2 pH measurements

A ROSS (Orion) combination pH electrode calibrated against standard buffers (pH 8–12) was used for the measurement of the proton concentration ($pH_m = -\log[H^+]$, with $[H^+]$ in molal scale). pH_m values were calculated from the measured pH_{exp} according to $pH_m = pH_{exp} + A_m$ with A_m being empirical correction factors entailing both the liquid junction potential of the electrode and the activity coefficient of H^+. A_m values as a function of the electrolyte concentration for systems with $I \geq 0.1$ mol kg^{-1} can be expressed empirically by polynomial functions previously reported in Altmaier et al. (2003) (NaCl and $MgCl_2$ systems) and Altmaier et al. (2008) ($CaCl_2$ system) [14, 44].

2.3 Preparation and characterization of the solid phases

The solid phase $Nd(OH)_3$(s) used for the solubility experiments with Nd(III) was prepared under Ar atmosphere by hydration of crystalline Nd_2O_3(cr) in Milli-Q water during three months. The same synthesis route was used by Neck et al. (2009), and the solubility data reported there are used in this work as ligand-free baseline values.

An aged (≈eight years), nano-crystalline thorium hydroxide solid phase, ThO_2(ncr, hyd), was used in the solubility experiments with Th(IV). The original solid phase was prepared by slow addition of 0.1 M NaOH to a 0.25 M thorium nitrate solution (10 ml) under gentle agitation. The white precipitate was washed several times with water until nitrate was completely removed, and stored in a glove box under Ar atmosphere.

Metaschoepite, $UO_3{\cdot}2H_2O$(cr), was prepared by slow addition of 0.01 M NaOH to a 0.65 M uranium nitrate solution (2 ml) under gentle agitation. The pH was maintained below five to obtain the quantitative precipitation of metaschoepite and avoid the formation of Na-uranates [45, 46]. The resulting yellow solid phase was aged for one week and washed several times with water until nitrate was completely removed from solution. Sodium diuranate, $Na_2U_2O_7{\cdot}H_2O$(cr), was prepared following the protocol described in Altmaier et al. (2017) [46]. A suspension of metaschoepite synthesized as described above was titrated to pH = 11 with NaOH. The solid phase transformation was completed within one week, resulting in an intense yellow–orange compound. The resulting solid phase was aged for several months in a 1.0 M NaCl solution at $pH_m = 11$. Calcium uranate, $CaU_2O_7{\cdot}3H_2O$(cr), was prepared as described in Altmaier et al. (2005) [47]. Briefly, metaschoepite was equilibrated in a 1.0 M $CaCl_2$ solution at $pH_m \approx 11$. The transformation was complete after 50 days.

The synthesized solid phases were characterized by X-ray diffraction (XRD) before starting the solubility experiments. Diffraction patterns were collected with a Bruker AXS D8 Advance X-ray powder diffractometer at $5 \leq 2\Theta \leq 60°$ with a step size of 0.01–0.04° and measurement time of 9–55 s per step. Figure 2 shows a comparison of the XRD patterns of the solid phases considered in this work with reference data available in the JCPDS database [48] and in the literature. The characteristic peaks positions of ThO_2(s), $Nd(OH)_3$(s), $Na_2U_2O_7{\cdot}H_2O$(cr) and $UO_3{\cdot}2H_2O$(cr) are in excellent agreement with the corresponding JCPDS reference files (ThO_2(cr) JCPDS file no. 75-0052; $Nd(OH)_3$(cr) JCPDS file no. 70-0215; $Na_2U_2O_7{\cdot}H_2O$(cr) JCPDS file no. 43-0347; $UO_3{\cdot}2H_2O$(cr) JCPDS file no. 43-0364). Due to the relatively long ageing time of eight years, the Th(IV) hydrous oxide used in this work reveals a significant degree of crystallinity and for this reason is quoted as ThO_2(ncr, hyd) in the text below. Although several calcium uranate solid phases are included in the XRD reference database JCPDS (49-1050, 05-0606, 20-0245, 44-0583, 37-0496, 22-0335, 45-0008, 22-0817, 20-1327) no appropriate XRD reference pattern matching that of the solid phase synthesized in this work is available. However, the comparison with XRD data reported by Altmaier et al. confirms the predominance of the uranate phase $CaU_2O_7{\cdot}3H_2O$(cr) [47].

2.4 Solubility experiments

The solubility of $Nd(OH)_3$(s), ThO_2(ncr, hyd), $UO_3{\cdot}2H_2O$(cr), $Na_2U_2O_7{\cdot}H_2O$(cr) and $CaU_2O_7{\cdot}3H_2O$(cr) solid phases was studied in the presence of adipic acid ($C_6H_{10}O_4$), methyl acrylate ($C_4H_6O_2$), citric acid (Cit, $C_6H_8O_7$), melamine ($C_3H_6N_6$), ethylene glycol ($C_2H_6O_2$), phthalic acid ($C_8H_6O_4$) and gluconic acid (GLU, $C_6H_{12}O_7$). Solubility experiments were performed from undersaturation conditions. The solid phases were equilibrated in independent batch samples with

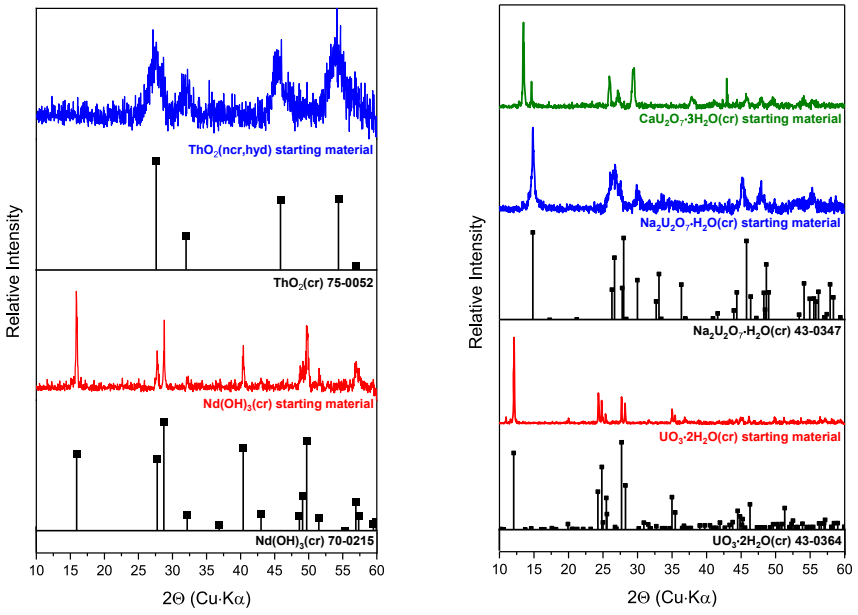


Figure 2: X-ray diffraction (XRD) patterns of the solid phases used in the solubility experiments. Left: $Nd(OH)_3$(s) and ThO_2(ncr, hyd). Right: metaschoepite $UO_3{\cdot}2H_2O$(cr), sodium uranate $Na_2U_2O_7{\cdot}H_2O$(cr) and calcium uranate $CaU_2O_7{\cdot}3H_2O$(cr). Squares represent peak positions and relative intensities of $Nd(OH)_3$(cr) (JCPDS file no. 70-0215), ThO_2(cr) (JCPDS file no. 75-0052), $UO_3{\cdot}2H_2O$(cr) (JCPDS file no. 43-0364) and $Na_2U_2O_7{\cdot}H_2O$(cr) (JCPDS file no. 43-0347).

2.63 and 5.61 m NaCl (pH_m = 9, 13), 1.03 and 3.87 m $MgCl_2$ (pH_m = 9) and 1.02 and 3.91 m $CaCl_2$ (pH_m = 9, 12) containing one of the above-mentioned ligands. The experimental conditions are summarized in Table 1.

The ligand concentration was fixed at 0.025 M for all ligands except adipic acid, melamine and phthalic acid. Due to the reduced water solubility of these ligands, lower concentrations (0.001–0.003 M) were used. Furthermore, no samples with citrate were prepared in $CaCl_2$ solutions because of the expected precipitation of the sparingly soluble $Ca_3Cit_2{\cdot}4H_2O$(cr) [49–52].

pH_m and [Nd], [Th] and [U] were analysed at regular time intervals from 12 to 181 days. After phase separation by ultrafiltration with 10 kDa filters (Pall Life science) the original samples were diluted 1:125–1:500 times (depending on electrolyte concentration) with 2% HNO_3 and the concentrations of Nd, Th-232 and U-238 measured by ICP-MS (inductively coupled plasma mass spectrometry, Perkin Elmer ELAN 6100). Blank measurements of 2% HNO_3 samples are used for the calculation of the detection limits which range from ~ 10^{-8} to ~10^{-10} M (depending on the dilution factor).

2.5 Thermodynamic data used in the present work

The solubility of Nd(III), Th(IV) and U(VI) in the presence of selected organic ligands is compared with correspondent thermodynamic calculations for the ligand-free systems. Solubility curves of Nd(III), Th(IV) and U(VI) are calculated using the thermodynamic data reported in Neck et al. [13], the Nuclear Energy Agency-Thermochemical Database (NEA-TDB) review on Th [53] and Altmaier et al. [46], respectively. Since no thermodynamic model for U(VI) in $CaCl_2$ solutions is available yet, the results obtained in this work for this system are directly compared with experimental data reported in Altmaier et al. for the analogous ligand-free systems [47, 54].

The specific ion interaction theory (SIT) has been used for the calculation of the solubility of Nd(III), Th(IV) and U(VI) in the absence of any organic ligand at a given electrolyte concentration and pH [55]. According to the SIT, the conditional equilibrium constant $\log^* K'$ is related to $\log^* K^0$ representing the equilibrium constant at infinite dilution (I = 0) by

$$\log^* K' = \log^* K^0 + \Delta z^2 D - \Delta\epsilon \cdot [X] - n\log a_w \quad (1)$$

where $\Delta z^2 = \sum z^2(\text{products}) - \sum z^2(\text{educts})$, D is the Debye–Hückel term $D = 0.509\sqrt{I_m}/(1 + 1.5\sqrt{I_m})$ at 25 °C, $\Delta\epsilon = \sum\epsilon_{ij}(\text{products}) - \sum\epsilon_{ij}(\text{educts})$ with ε_{ij} representing the SIT ion interaction parameters for a pair of oppositely charged ions, $[X]$ is the concentration of the counter ion in the background electrolyte and a_w the water activity for a given electrolyte concentration. The values for $\log^* K^0$ and ε_{ij} for the different species used for the calculation of the solubility curves of Nd(III), Th(IV) and U(VI) in the absence of any organic ligand are summarized in Tables A1 and A2 in the Supplementary Material.

Table 1: Summary of the experimental conditions (electrolyte concentration, pH_m, and solid phase) used in the solubility experiments.

Electrolyte	c [m]	pH_m	Nd(III) solid phase	Th(IV) solid phase	U(VI) solid phase
NaCl	2.63	≈9, ≈13	$Nd(OH)_3$(s)	ThO_2(ncr, hyd)	$Na_2U_2O_7{\cdot}H_2O$(cr)
	5.61	≈9, ≈13			
$MgCl_2$	1.03	≈9	$Nd(OH)_3$(s)	ThO_2(ncr, hyd)	$UO_3{\cdot}2H_2O$(cr)
	3.87	≈9			
$CaCl_2$	1.02	≈9, ≈12	$Nd(OH)_3$(s)	ThO_2(ncr, hyd)	$CaU_2O_7{\cdot}3H_2O$(cr)
	3.91	≈9, ≈12			

No SIT activity model is available for the system U(VI) in $MgCl_2$ solutions, and thus solubility calculations for this system in the absence of organic ligands are performed using the Pitzer activity model derived in Yalcintas et al. [56].

3 Results and discussion

3.1 Solubility of Nd(III)

Experimental solubility data determined for $Nd(OH)_3(s)$ in NaCl, $CaCl_2$ and $MgCl_2$ solutions in the presence of melamine, phthalate, citrate, adipate, methyl acrylate and ethylene are shown in Figure 3. The results are compared with experimental data and thermodynamic calculations reported in Neck et al. for analogous systems but in the absence of organic ligands [13].

Solubility data in Figure 3 show that melamine, phthalate, adipate, methyl acrylate and ethylene glycol have no significant impact on the solubility of $Nd(OH)_3(s)$ in the investigated NaCl, $MgCl_2$ and $CaCl_2$ systems. The formation of complexes of Nd(III) (or other lanthanides) with adipate and phthalate has been previously reported in the literature [57–60]. Thermodynamic data for the complexes of Eu(III) with phthalate ($Eu(pht)^+$ and $Eu(pht)_2^-$) are also selected in the ThermoChimie database [61]. However, the reported complexes have been studied under acidic conditions, and cannot outcompete Nd(III) hydrolysis in the alkaline to hyperalkaline conditions relevant in cementitious systems.

Citrate is the only ligand showing a significant effect on the solubility of $Nd(OH)_3(s)$ in NaCl solutions. The solubility enhancement is only observed at $pH_m \approx 9–10$, whereas virtually no effect arises at $pH_m \approx 13$. This behaviour is related to the different speciation of Nd(III) under these conditions, as well as to the strong competition with hydroxide expected at $pH_m \approx 13$. Citrate induces a slight increase in the solubility of Nd(III) in 1.03 m $MgCl_2$ solutions at $pH_m \approx 9$, whereas no effect is observed in 3.87 m $MgCl_2$ systems. This observation reflects the formation of Mg-citrate complexes, which are able to outcompete the complexation of Nd(III) with citrate in concentrated $MgCl_2$ solutions. Hence, the formation of the binary complex $Mg(cit)^-$ reduces the concentration of free citrate available for complexation with Nd(III) [49], and has to be considered for a quantitative evaluation of solubility data of Nd(III) in the presence of citrate in $MgCl_2$ solutions.

Several experimental studies describing the interaction of trivalent lanthanides and actinides (Eu(III), Nd(III), Cm(III), Am(III) etc.) with citrate are available in the

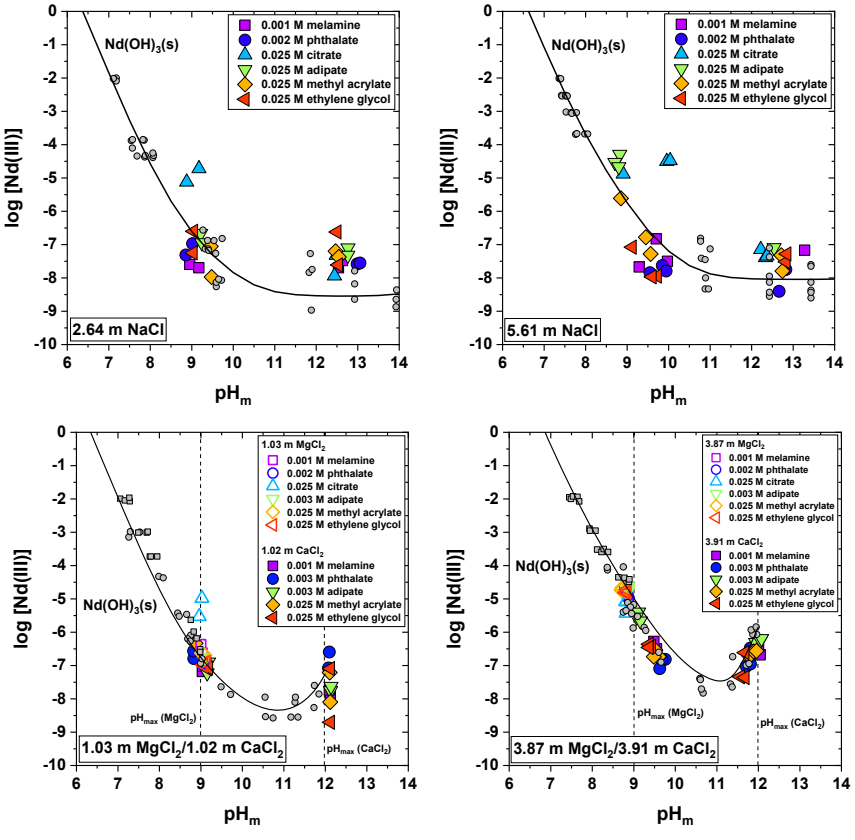


Figure 3: Experimental solubility data of Nd(III) in the presence of melamine, phthalate, citrate, adipate, methyl acrylate and ethylene glycol in NaCl (2.64 and 5.61 m, top), $MgCl_2$ (1.03 and 3.87 m, bottom) and $CaCl_2$ (1.02 and 3.91 m, bottom) solutions. Grey symbols represent experimental data for the solubility of $Nd(OH)_3(s)$ in the ligand-free system (Neck et al. [13]). Solid lines refer to the calculated solubility of $Nd(OH)_3(s)$ in the absence of any ligand using the thermodynamic and (SIT) activity models reported in Neck et al. [13].

literature [62–65]. However, most of these studies focus on acidic conditions and give no information about the complexation behaviour of Ln(III)/An(III) in the alkaline to hyperalkaline systems of relevance for cementitious environments. Svoronos et al. studied the complexation of Nd(III) with citrate in the pH range 1–13 by means of potentiometric titrations [66]. Based on the fit of their potentiometric data, the authors reported the formation of the complexes $NdCit_2^{3-}$, $Nd(OH)Cit^-$ and $Nd_3(OH)_4Cit_4^{7-}$ in the alkaline region, with $Nd_3(OH)_4Cit_4^{7-}$ being the species dominating at pH ≥ 8. Although the formation of ternary complexes Nd(III)-OH-Cit is to be expected in alkaline pH conditions, relevant flaws are identified in the experiments by Svoronos and co-workers under these conditions. Most importantly, the very high Nd(III) concentrations used in the potentiometric titrations ($4.3{\cdot}10^{-3}$–$2.2{\cdot}10^{-3}$ M) result in largely oversaturated conditions with respect to $Nd(OH)_3$(s), and thus the reported speciation scheme and equilibrium constants (in alkaline conditions) are not representative of equilibrium conditions.

3.2 Solubility of Th(IV)

Figure 4 shows the Th(IV) solubility data in NaCl, $MgCl_2$ and $CaCl_2$ systems in the presence of the investigated organic ligands. The figure shows also the solubility of Th(IV) calculated using the thermodynamic and SIT activity models reported in Rand et al. (2008) [53] and Altmaier et al. (2008) [14]. Note that thermodynamic calculations in Figure 4 have been performed using ThO_2(am, hyd, aged) as solid phase controlling the solubility of Th(IV).

Analogously to the experimental observations in the Nd(III) system, melamine, phthalate, adipate, methyl acrylate and ethylene glycol have no significant effect on the solubility of ThO_2(ncr, hyd) in the investigated NaCl, $MgCl_2$ and $CaCl_2$ systems.

On the contrary, citrate and gluconate significantly increase the solubility of ThO_2(ncr, hyd) in alkaline NaCl solutions. In the case of citrate, this effect is only observed for the samples at $pH_m \approx 9$, for which the solubility is enhanced 2–3 orders of magnitude with respect to the calculated citrate-free systems. Felmy et al. reported similar observations for the solubility of Th(IV) in the presence of citrate in 0.5–6.0 M $NaNO_3$ solutions at $5 \leq pH_m \leq 12$ [35]. The very significant increase in the solubility within the pH_m range 6–8 and the systematic decrease of this effect with increasing pH_m was described by the formation of a ternary Th(IV)-OH-cit complex (either $Th(OH)_3(cit)_3^{8-}$/$Th(H_{-1}cit)_3^{8-}$ or $Th(OH)_3(cit)_2^{5-}$/$Th(H_{-1}cit)_2^{5-}$). Because of the uncertainties in the stoichiometry of the complexes prevailing in solution and the high charge of these complexes, the authors were only able to provide maximum apparent equilibrium constants for the formation of the thorium citrate complexes.

In contrast to the citrate system, the effect of gluconate in NaCl systems is mostly observed at $pH_m \approx 13$. The different behaviour observed at $pH_m \approx 9$ and $pH_m \approx 13$ suggests that two different Th(IV)-GLU complexes prevail in these conditions, and that a different number of protons are involved in the equilibrium reactions controlling the solubility of Th(IV) in these conditions. In a systematic solubility study with Th(IV) in the presence of gluconate, Colàs et al. described the formation of a single complex with stoichiometry $Th(OH)_4(GLU)^-$ in $NaClO_4$ solutions up to pH 12 [36]. The observations by Colàs and co-workers are not necessarily in disagreement with our experimental results, considering the differences in the highest pH_m reached in both studies. Felmy et al. investigated the solubility of Th(IV) in the presence of gluconate within the pH range 4–12. At constant gluconate concentration, the authors observed a clear dependency of the solubility on pH, which hinted to the formation of (at least) two different aqueous complexes of Th(IV) with gluconate. Solubility data reported by Felmy and co-workers were later evaluated by Gaona et al., who proposed a chemical and thermodynamic model including the formation of the complexes $Th(OH)_4GLU^-$ and $Th(OH)_4GLU_{-H}^{2-}$. Due to the absence of solubility experiments at varying gluconate concentration the latter authors acknowledged that the solubility dataset could be equally explained with the aqueous complexes $Th(OH)_4GLU_2^{2-}$ and $Th(OH)_4(GLU)(GLU_{-H})^{3-}$ [34, 68]. Although the pH range and background electrolyte investigated in Felmy et al. do not perfectly match the conditions of the present work, an increasing solubility with increasing pH is observed in both studies hinting in both cases to the formation of at least two Th(IV) gluconate species under alkaline conditions. Since the presence of the α-hydroxyl group seems to be a key feature for both gluconate and citrate the formation of the $Th(OH)_4GLU_{-H}^{2-}$ species is very likely under alkaline conditions.

The solubility of ThO_2(ncr, hyd) in 1.03 and 3.87 m $MgCl_2$ at $pH_m \approx 9$ is only increased in the presence of citrate and gluconate (Figure 4) thus supporting the formation of Th(IV)-cit and Th(IV)-GLU complexes also in $MgCl_2$ systems. For citrate, the increase in solubility is slightly lower compared to the NaCl systems at $pH_m \approx 9$, which possibly reflects the competition with binary Mg-cit complexes. On the contrary, a slight increase in solubility with respect to analogous NaCl systems is observed for gluconate case.

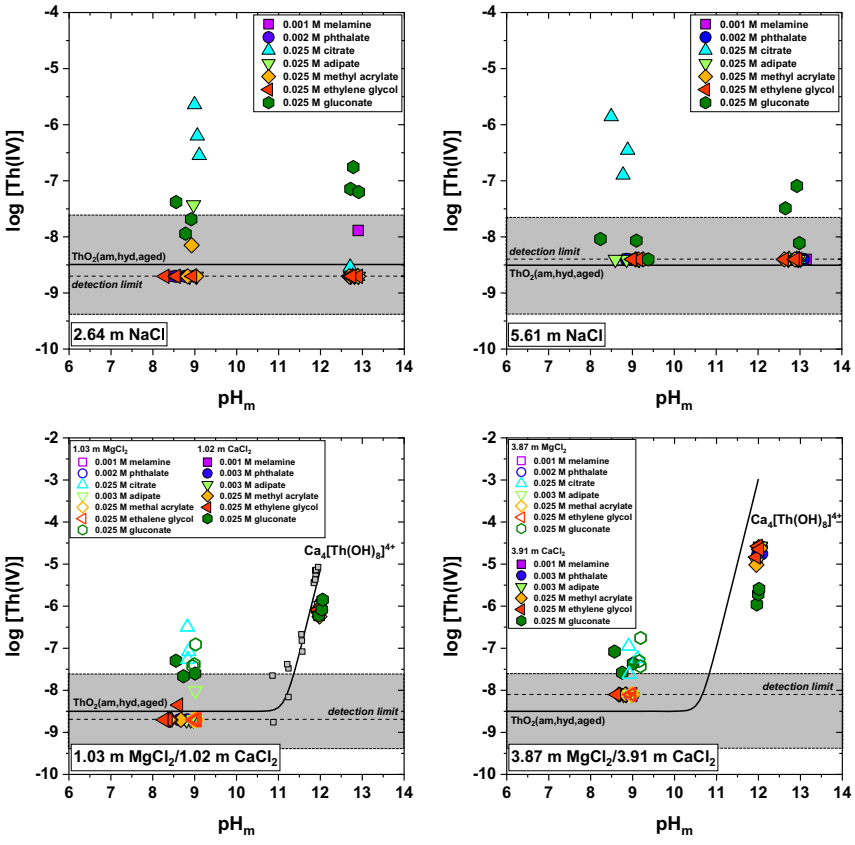


Figure 4: Experimental solubility data of Th(IV) in the presence of melamine, phthalate, citrate, adipate, methyl acrylate, ethylene glycol and gluconate in NaCl (2.64 and 5.61 m, top), $MgCl_2$ (1.03 and 3.87 m, bottom) and $CaCl_2$ (1.02 and 3.91 m, bottom) solutions. Shadowed grey areas are regions of constant Th(IV) concentration in the ligand-free systems [67]. Grey symbols represent experimental data for the solubility of ThO_2(am, hyd) in the ligand-free system (Altmaier et al. [14]). Solid lines refer to the calculated solubility of ThO_2(am, hyd, aged) in the absence of any ligand using the thermodynamic and SIT activity models reported in Rand et al. and Altmaier et al. [14, 53].

This observation may hint to the formation of ternary Mg-Th(IV)-GLU complexes, although additional experimental evidences are required to validate this hypothesis.

Gluconate is the only ligand enhancing the solubility of Th(IV) in 1.02 and 3.91 m $CaCl_2$ solutions at $pH_m \approx 9$, whereas at this pH_m the solubility remains mostly unaffected for all other ligands (Figure 4). The solubility is slightly higher than for the analogous NaCl system at $pH_m \approx 9$, which may hint to the formation of ternary Ca-Th(IV)-GLU complexes as proposed for the $MgCl_2$ system. The increase in solubility observed at $pH_m \approx 12$ with respect to data at $pH_m \approx 9$ is not attributed to the complexation with gluconate, but rather corresponds to the formation of the ternary complex $Ca_4[Th(OH)_8]^{4+}$, as previously reported in Altmaier et al. The decreased solubility observed for all ligands with respect to the ligand-free system (especially at high ionic strength conditions) can be explained by the higher crystallinity of the solid phase used in the present work, ThO_2(ncr, hyd), expectedly holding a lower solubility than the amorphous phase used by Altmaier et al. or selected in the NEA-TDB [14, 53]. The presence of gluconate results in a significant decrease of the solubility in 3.91 m $CaCl_2$ solutions at $pH_m \approx 12$, with respect to all other ligand systems. Two hypothesis can be raised to explain these observations: (i) formation of a quaternary solid phase Ca-Th(IV)-OH-GLU with the consequent decrease in solubility, or (ii) slight decrease in pH_m as a result of the formation of ternary Ca-OH-GLU complexes in solution (*e.g.* $Ca_3(OH)_3GLU_2^+$ or $Ca_3(OH)_4GLU_2$(aq)) [69]. Note that in this pH_m-region, a decrease of 0.1 pH_m-units results in a decrease in 0.4 $\log_{10}$-units in the concentration of Th(IV) due to the steep slope (+4) of the solubility curve.

The differences observed in $CaCl_2$ systems with gluconate at $pH_m \approx 9$ and $pH_m \approx 12$ can be largely attributed to the different speciation of the binary systems Th(IV)-$CaCl_2$ and GLU-$CaCl_2$ at these pH_m-values. Hence, $Th(OH)_4$(aq) and the (weak) complex $CaGLU^+$ prevail at $pH_m \approx 9$, whereas the very stable complexes $Ca_4Th(OH)_8^{4+}$ and $Ca_3(OH)_4GLU_2$(aq) dominate at $pH_m \approx 12$.

Only a limited number of experimental studies have investigated the interaction of Th(IV) with gluconate in the presence of Ca, all of them focussing on low ionic strength conditions. Tits et al. studied the sorption of Th(IV) onto calcite in the presence of gluconate. Experiments were performed in artificial cement pore water at pH = 13.3 containing $[Ca]_{tot} = 1.6 \cdot 10^{-3}$ M. Based on the decrease of the sorption with increasing ligand concentration, the authors derived chemical and thermodynamic models including the only formation of a ternary Ca-Th(IV)-GLU complex, $CaTh(OH)_4GLU_2$(aq) [33, 34]. Sorption experiments were

conducted at constant pH and [Ca], and thus the stoichiometry of the complex was assumed based on the analogy with a previous study on the system Ca-Th(IV)-ISA [70]. The very different behaviour observed for the system Ca-Th(IV)-GLU in Tits et al. and in the present work under similar pH conditions (13.3 *vs.* 13) supports again the difficulty of extrapolating experimental data obtained at low ionic strength to intermediate/high ionic strength conditions. Bond and Tweed, Baston et al. and Berry et al. studied the influence of gluconate on the sorption of Th(IV) onto London clay, Caithness flagstones, St Bees sandstone and Borrowdale volcanic rocks in alkaline, calcium containing solutions [71–74]. No clear evidence on the formation of ternary Ca-Th(IV)-GLU complexes was obtained, but the slight sorption reduction observed for certain experiments was attributed to the possible sorption of such complexes on the investigated solid phases.

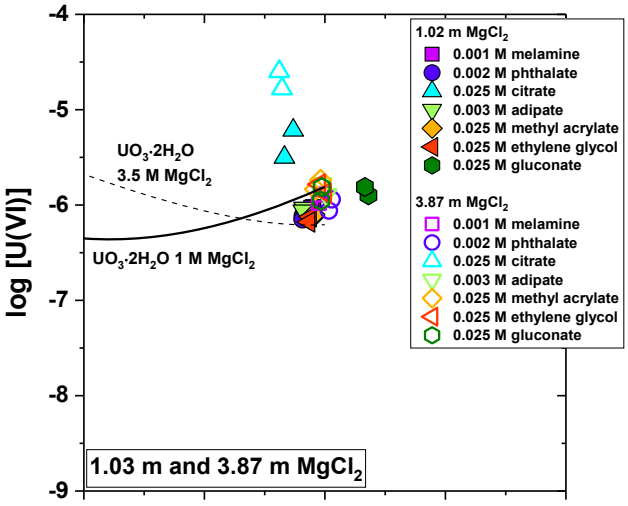


Figure 6: Experimental solubility data of U(VI) in the presence of melamine, phthalate, citrate, adipate, methyl acrylate, ethylene glycol and gluconate in 1.03 m (filled symbols) and 3.87 m (open symbols) $MgCl_2$ solutions. Lines refer to the calculated solubility of $UO_3{\cdot}2H_2O$(cr) in the absence of any ligand using the thermodynamic and Pitzer activity models reported in Yalcintas et al. (solid line: 1.03 m $MgCl_2$, dashed line: 3.87 m $MgCl_2$).

3.3 Solubility of U(VI)

Figures 5–7 show the U(VI) solubility data in NaCl, $MgCl_2$ and $CaCl_2$ systems, respectively, in the presence of the investigated organic ligands. The figures show experimental solubility data and thermodynamic calculations for the ligand-free systems as reported in Altmaier et al. (2017), Yalcintas et al. (2019) and Altmaier et al. (2005).

Melamine, phthalate, adipate, methyl acrylate and ethylene glycol have no effect on the solubility of U(VI) in 2.64 and 5.61 m NaCl solutions (Figure 5). This is in line with the results obtained for the Nd(III) and Th(IV) systems, thus highlighting the minor impact that these ligands have on the solution chemistry of actinides and lanthanides in alkaline conditions. Citrate and gluconate significantly increase the solubility of U(VI) in NaCl solutions at $pH_m \approx 9$, with the effect being more pronounced at lower ionic strength conditions. On the contrary, neither citrate nor

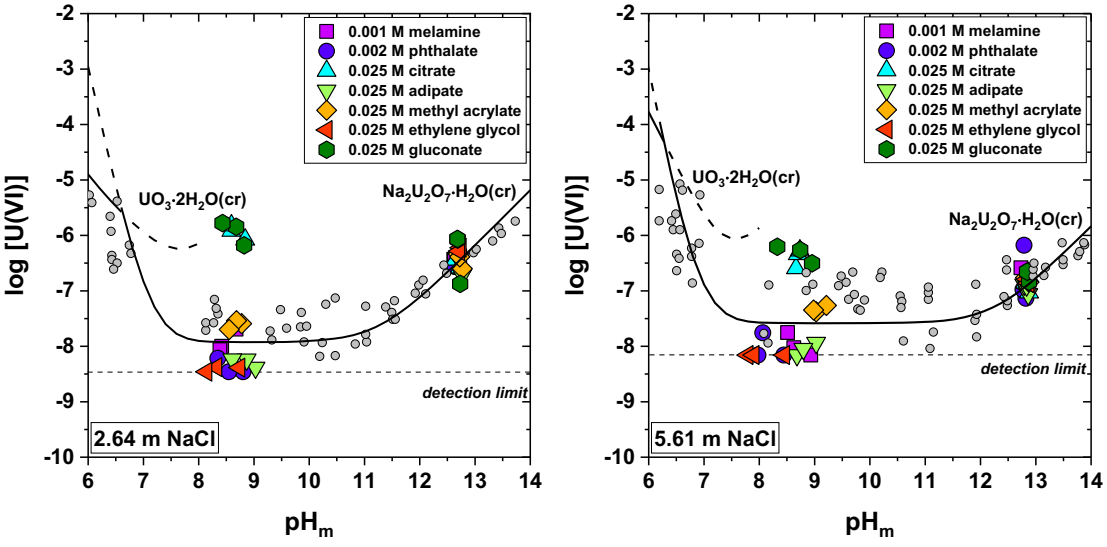


Figure 5: Experimental solubility data of U(VI) in the presence of melamine, phthalate, citrate, adipate, methyl acrylate, ethylene glycol and gluconate in 2.64 and 5.61 m NaCl solution. Grey symbols represent experimental data for the solubility of $UO_3{\cdot}2H_2O$(cr) and $Na_2U_2O_7{\cdot}H_2O$(cr) in 2.64 and 5.61 m NaCl in the ligand-free system (Altmaier et al. [46]). Solid lines refer to the calculated solubility of $UO_3{\cdot}2H_2O$(cr) and $Na_2U_2O_7{\cdot}H_2O$(cr) in the absence of any ligand using the SIT model of Altmaier et al. [46].

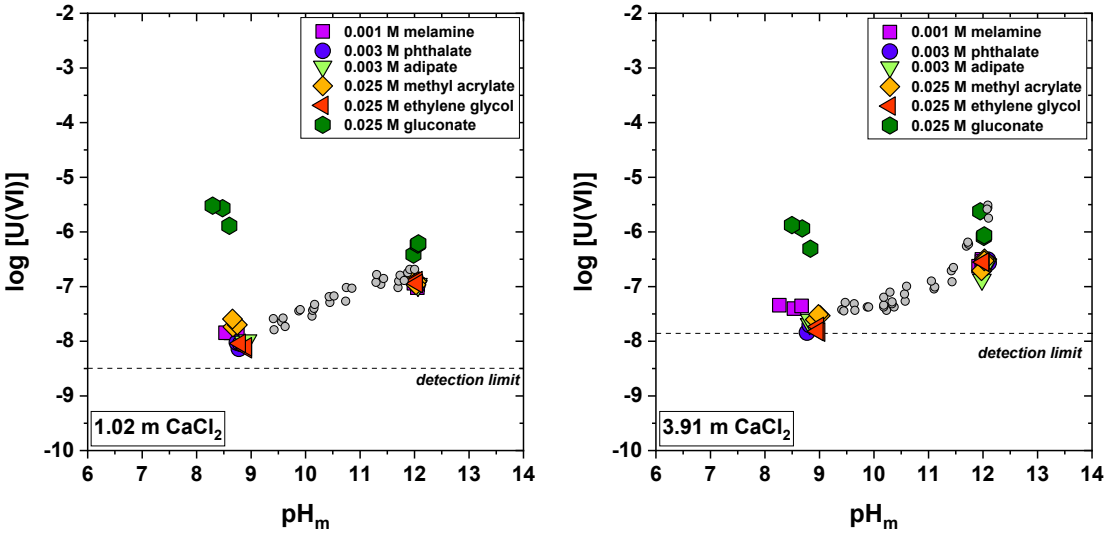


Figure 7: Experimental solubility data of U(VI) in the presence of melamine, phthalate, adipate, methyl acrylate, ethylene glycol and gluconate in 1.02 m (left) and 3.91 m (right) $CaCl_2$ solution. Grey symbols represent experimental data for the solubility of $CaU_2O_7{\cdot}3H_2O$(cr) in 1.02 and 4.0 m $CaCl_2$ in the ligand-free system (Altmaier et al. [54]).

gluconate induce any solubility enhancement at $pH_m \approx 13$. These observations are likely related to the differences in the aqueous speciation of U(VI) at $pH_m \approx 9$ and 13, dominated (in the absence of organic ligands) by $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$, respectively.

Several publications describing the interaction of U(VI) with gluconate in the acidic pH range are available in the literature [75], but only very few studies focus on high pH conditions. All the available studies were conducted at $I \leq 1.0$ M. Colas et al. investigated the influence of gluconate on the solubility of U(VI) in 0.5 M KCl solutions at fixed $pH_m = 12$ [76]. The authors observed a solubility enhancement and proposed the formation of a ternary U(VI)-OH-gluconate complex, $UO_2(OH)_2(GLU_{-H})^{2-}$. The same complex was previously reported by Sawyer et al. based on a series of spectroscopic, polarographic, polarimetric and potentiometric studies within $2 \leq pH \leq 14$ [77]. Note however that the proposed stoichiometry assumed the predominance of the complex UO_2OH^+ in the absence of gluconate, which is erroneous for most of the pH-conditions investigated by the authors. Spectroscopic data reported by Sawyer and co-workers confirmed that the U(VI)-gluconate complexes are not stable at pH = 14, which is in line with the observations in the present study at $pH_m = 13$. Baston et al. and Berry et al. investigated the sorption of U(VI) onto London clay, Caithness flagstones, St Bees sandstone and Borrowdale volcanic rocks in the presence of gluconate at $8 \leq pH \leq 11$ [73, 74]. The authors reported a decrease of the sorption in the presence of gluconate compared to ligand-free systems, which was attributed to the formation of aqueous U(VI) gluconate complexes.

The speciation of the uranyl citrate system has been extensively studied by using different instrumental techniques during the last decades, and the formation of very stable mono- and polynuclear species is reported. There is a general agreement on the formation of monomeric $UO_2(Cit)H_n^{n-1}$ (with n = 0, 1, 2, 3) and dimeric $(UO_2)_2(Cit)_2(OH)_n^{-(n+2)}$ (with n = 0, 1, 2) species up to pH ≈ 5, although only three U(VI)-Cit complexes are currently selected in the NEA-TDB reviews, *i.e.* $UO_2(Cit)^-$, $UO_2(HCit)(aq)$ and $(UO_2)_2(Cit)_2^{2-}$. Beyond the well-stablished formation of monomeric and dimeric complexes, the predominance of trimeric (or hexameric) species under near-neutral pH conditions has also been proposed [78–81]. However, data describing the interaction of U(VI) with citrate under alkaline conditions are rare. Barger et al. reported a decrease of U(VI) sorption onto kaolinite in the presence of citrate between pH_m 5 and 10 [82]. These observations are in line with the increase in solubility observed in the present study at $pH_m \approx 9$, thus supporting the formation of U(VI)-citrate complexes also in weakly alkaline systems. Pasilis et al. studied the interaction of U(VI) with citrate using Raman spectroscopy up to pH = 9.5, and proposed the predominance of the complex $[(UO_2)_3(Cit)_3]^{3-}$ under alkaline conditions [83]. Note however that much higher U(VI) concentrations were used by the latter authors ($5{\cdot}10^{-4} \leq [U(VI)] \leq 0.05$ M) compared to the concentration

levels determined in the current undersaturation solubility experiments ([U(VI)] ≤ $5{\cdot}10^{-6}$ M, in equilibrium with $Na_2U_2O_7{\cdot}H_2O$(cr)).

Citrate is the only ligand significantly enhancing the solubility of U(VI) in 1.03 and 3.87 m $MgCl_2$ solutions with $pH_m \approx 9$ (Figure 6). The observed increase in solubility agrees well with the behaviour of U(VI) in the presence of citrate in NaCl solutions of similar pH_m conditions. In contrast to the NaCl system, the effect of citrate in $MgCl_2$ systems is more pronounced under high ionic strength conditions. This can be explained by (i) the change in the speciation of U(VI) between 1.03 $MgCl_2$ (predominance of anionic hydrolysis species) and 3.87 m $MgCl_2$ (predominance of cationic hydrolysis species) solutions, and/or (ii) the possible formation of ternary complexes Mg-U(VI)-citrate. Additional experimental and theoretical studies are required to provide conclusive insights in the complexation phenomena within the ternary system Mg-U(VI)-citrate.

The absence of any effect of gluconate in the solubility of U(VI) in $MgCl_2$ systems appears *a priori* unexpected. Binary Mg-gluconate complexes forming in weakly alkaline systems with [Mg] ≤ 0.1 M are relatively weak ($\log\beta_1$ = 0.2–0.7) [84]. These observations reflect again the difficulties in extrapolating results obtained at low ionic strength conditions to intermediate/high ionic strength systems, as well as the importance of having an accurate knowledge of the binary system M(II)-L to allow the correct interpretation and prediction of the radionuclide behaviour in the ternary systems M(II)-An-L.

Gluconate is the only ligand significantly enhancing the solubility of U(VI) in $CaCl_2$ solutions with $pH_m \approx 9$ (Figure 7). This effect differs from the results obtained in $MgCl_2$ systems of analogous pH_m and ionic strength. Considering that the binary complexes Ca-GLU are significantly stronger than the Mg-GLU counterparts, this observation points towards the likely formation of previously unreported Ca-U(VI)-GLU ternary complexes. This hypothesis is also in line with the proposed formation of ternary Ca-An(IV)-GLU and Ca-An(III)/Ln(III)-GLU complexes [33, 85, 86]. In contrast to the results obtained at $pH_m \approx 9$, gluconate has no (or only a weak) effect on the solubility of U(VI) in $CaCl_2$ solutions with $pH_m \approx 12$. This is consistent with observations in NaCl systems, where gluconate showed only a clear effect on the solubility of $Na_2U_2O_7{\cdot}H_2O$(cr) at $pH_m \approx 9$. Note that in addition to the highly hydrolysed moiety of U(VI) dominating at $pH_m \approx 13$ gluconate forms very stable binary Ca-GLU and ternary Ca-GLU-OH complexes (CaGLU(OH) and $Ca_3GLU_2(OH)_4$) importantly decreasing the concentration of free gluconate available for U(VI) complexation at $pH_m \geq 11$ [87].

4 Summary and conclusions

The impact of selected cement additives and model compounds on the solubility of Nd(III), Th(IV) and U(VI) was quantitatively evaluated with a series of screening experiments in alkaline NaCl, $MgCl_2$ and $CaCl_2$ solutions of elevated ionic strength ($2.5 \leq I \leq 10.5$ M).

Most of the investigated ligands (melamine, phthalate, adipate, methyl acrylate, ethylene glycol) have no impact on the solubility lanthanides and actinides within the investigated conditions, in spite of the variety of functional groups represented by these compounds (alcohol, amine, carboxylic). On the contrary, citrate and gluconate induce a systematic increase in the solubility for most of the investigated systems. These observations hint to the presence of both alcohol and carboxylic groups in the organic ligand as key parameter for the formation of stable (chelate) complexes with lanthanides and actinides in alkaline to hyperalkaline conditions.

Citrate enhances the solubility of Nd(III) mostly in NaCl systems and at $pH_m \approx 9$. The complexation of Nd(III) with citrate is almost completely outcompeted in the presence of Mg, whereas at $pH_m \approx 13$ the hydrolysis species $Nd(OH)_3$(aq) prevails over any Nd(III)-citrate complex.

Both gluconate and citrate increase the solubility of Th(IV) in NaCl solutions. The pH-dependency of the forming complexes is however opposite, with citrate complexes being more stable at $pH_m \approx 9$ and gluconate ones at $pH_m \approx 13$. These differences are explained by the number of alcohol groups in each ligand (one in citrate, five in gluconate) sensitive to be deprotonated at $pH_m \approx 13$. The formation of binary Mg(II)-citrate complexes decreases the impact of this ligand on the solubility of Th(IV), whereas the possible formation of ternary Mg/Ca-Th(IV)-GLU complexes is hinted for the gluconate system.

Citrate and gluconate induce a significant increase in the solubility of U(VI) at $pH_m \approx 9$ in NaCl, $MgCl_2$ and $CaCl_2$ (only for gluconate) systems. At this pH_m the relevant differences observed between $MgCl_2$ and $CaCl_2$ systems suggest the formation of ternary Ca-U(VI)-GLU complexes. Neither citrate nor gluconate lead to a significant effect in the solubility of U(VI) at $pH_m \approx 12$–13 in NaCl and $CaCl_2$ systems. This is explained by the predominance of a highly hydrolysed moiety in solution, $UO_2(OH)_4^{2-}$, which cannot be outcompeted by the formation of complexes with these ligands.

This study represents a key contribution to understand the role of organic cement additives and model compounds in the possible mobilization of An(III)/Ln(III), An(IV) and An(VI) under intermediate to high ionic strength conditions. Solubility data determined in this work provide

robust solubility upper limits that can be considered for source term estimations under geochemical boundary conditions relevant for specific host-rock formations. Experimental data collected in this work also highlight relevant differences with respect to dilute systems, in particular in the presence of the alkali-earth metals Mg and Ca. Dedicated experimental efforts are advisable for these systems, as extrapolation from low ionic strength conditions may result in gross errors.

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