Thermodynamics of trivalent actinides and neodymium in NaCl, MgCl$_2$, and CaCl$_2$ solutions: Solubility, hydrolysis, and ternary Ca–M(III)–OH complexes

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Abstract: Known data on the solubility of Am(OH)$_3$(s) and the hydrolysis of Am(III) and Cm(III), additional information from an extensive solubility study with Nd(OH)$_3$(s) in NaCl, MgCl$_2$, and CaCl$_2$ media of various ionic strengths and spectroscopic (time-resolved laser fluorescence spectroscopy, TRLFS) data for Cm(III) in alkaline CaCl$_2$ solutions are used to evaluate a comprehensive set of standard-state equilibrium constants and ion interaction parameters for the specific ion interaction theory (SIT) and Pitzer equations at 25 °C. The thermodynamic model takes into account the analogous solubility and hydrolysis behavior of trivalent actinides and Nd(III) and covers the entire pH range in dilute to concentrated NaCl, MgCl$_2$, and CaCl$_2$ solutions. In alkali chloride/hydroxide solutions, the formation of the tetrahydroxide complex M(OH)$_4^{2-}$ requires OH$^-$ concentration above 3 mol l$^{-1}$, whereas in alkaline CaCl$_2$ solutions (at pH$_c$ < 12) M(III) complexes with four and six hydroxide ligands are formed. Similar as the recently detected ternary Ca–M(IV)–OH complexes Ca$_3$[Zr(OH)$_6$]$^{4+}$ and Ca$_4$[Th(OH)$_8$]$^{4+}$, these complexes are stabilized by the association of Ca$^{2+}$ ions. The solubility and hydrolysis of Am(III), Cm(III), and Nd(III) in both Ca-free and -containing solutions is consistently described with a model including the ternary Ca–M(III)–OH complexes Ca[M(OH)$_3$]$^{2+}$, Ca$_2$[M(OH)$_4$]$^{3+}$, and Ca$_3$[M(OH)$_6$]$^{4+}$.

Keywords: americium; curium; hydrolysis; neodymium; Pitzer model; plutonium; SIT; solubility; ternary complexes.

INTRODUCTION

The solubility and aqueous speciation of actinides in chloride solutions is of particular interest with regard to the safety of nuclear waste storage in underground salt mines like the Waste Isolation Pilot Plant (WIPP) in the United States or the Asse salt mine in Germany. Intrusion of water is supposed to yield NaCl- or MgCl$_2$-dominated salt brines. In order to minimize actinide solubilities, brucite-based backfill material has been proposed to buffer pH by magnesium hydroxide Mg(OH)$_2$(s) or hydroxychloride Mg$_2$(OH)$_5$Cl·4H$_2$O(s) at values of pH = 9 [1,2] and to scavenge carbonate due to the limited solubility.
of magnesium carbonates. In MgCl$_2$ brines, the corrosion of cementitious waste forms can lead to CaCl$_2$-dominated solutions buffered at pH \( \approx 12 \) by calcium hydroxide Ca(OH)$_2$\( (s) \) or hydroxychlorides, Ca$_4$(OH)$_6$Cl$_2$\( \cdot 13\text{H}_2\text{O}(s) \) and Ca$_2$(OH)$_2$Cl$_2$\( \cdot \text{H}_2\text{O}(s) \) [2]. Under redox conditions controlled by corroding steel containers of nuclear waste packages, the most important actinides will be in the oxidation states An(III) (Am, Cm, Pu) or An(IV) (Th, U, Np, Pu) [3–7]; for plutonium, solid PuO$_2$(s, hyd) is expected in equilibrium with aqueous Pu(IV) and Pu(III) species [8].

Thermodynamic data for the solubility and hydrolysis of tri- and tetravalent actinides in chloride solutions belong to the key values for performance assessment calculations. However, the data selected in the critical reviews of the Organization for Economic Cooperation and Development (OECD)/Nuclear Energy Agency (NEA-TDB) [3–7] are usually based on experimental studies in NaClO$_4$ or NaCl media. There is a lack of systematic studies in dilute to concentrated MgCl$_2$ and CaCl$_2$ solutions. Moreover, our recent solubility measurements and spectroscopic studies with Zr(IV), Th(IV), Pu(IV), Nd(III), and Cm(III) in alkaline CaCl$_2$ solutions [9–12] revealed a hitherto unknown phenomenon, the formation of ternary Ca–M–OH complexes with unusually high numbers of OH$^-$ ligands. The solubilities of ZrO$_2$\( \cdot \text{xH}_2\text{O}(s) \) at pH = 10–12 in 0.1–2.0 M CaCl$_2$ and of ThO$_2$\( \cdot \text{xH}_2\text{O}(s) \) at pH = 11–12 in 0.5–4.5 M CaCl$_2$ are raised to unexpectedly high values by the formation of the complexes Ca$_3[Zr(OH)_{6}]^{4+}$ and Ca$_4[Th(OH)_{8}]^{4+}$, respectively, which could be identified and characterized by extended X-ray absorption fine structure spectroscopy (EXAFS) [9,10]. The equilibrium constants for these complexes were calculated in [10] with the specific ion interaction theory (SIT) [13] recommended in the NEA-TDB for ionic strength corrections. However, highly saline MgCl$_2$ or CaCl$_2$ solutions with ionic strengths up to 16 mol kg$^{-1}$ are far beyond the validity range of the SIT (\( I < 4 \text{ mol kg}^{-1} \)).

The ion interaction model of Pitzer [14] is applicable to high ionic strength and used in geochemical modeling codes like EQ3/6 or Geochemist’s Workbench (GWB). Therefore, it was recently used to model the data for the An(IV) complex Ca$_4[An(OH)_{8}]^{4+}$ (An = Th and Pu) at high CaCl$_2$ concentrations [12]. Standard-state equilibrium constants and ion interaction parameters for the An(III) species formed in neutral and alkaline NaCl, MgCl$_2$, and CaCl$_2$ solutions will be presented in this paper.

**SOLUBILITY AND HYDROLYSIS OF TRIVALENT ACTINIDES—STATE OF THE ART**

Trivalent actinides and lanthanides show pronounced analogies in most chemical properties, systematic trends in the thermodynamic data and equilibrium constants often correlate with the ionic radius [6,15,16]. Considering the similar ionic radii of Nd$^{3+}$, Pu$^{3+}$, Am$^{3+}$, and Cm$^{3+}$ (111, 112, 110, and 109 pm, respectively, at coordination number CN = 8 [16,17]), it is not surprising that the real differences between the formation constants of their aqueous complexes are smaller than the experimental uncertainties [6,18]. Due to specific experimental difficulties or the lack of appropriate experimental methods for Am(III) or Pu(III) at trace concentration levels, it is more convenient to use oxidation-state analogs, for instance, Cm(III) with fluorescence properties that allow investigations by time-resolved laser fluorescence spectroscopy (TRLFS) at concentrations below $10^{-7}$ mol l$^{-1}$ [19]. For reasons of easier handling, the non-radioactive lanthanides Nd(III) and Eu(III) are also often studied as analogs for the trivalent actinides.

The literature on the solubility and hydrolysis of Am(III), Cm(III), and Pu(III) is critically discussed in NEA-TDB reviews [4–6]. In the absence of carbonate, silicate, or phosphate, the solubility-limiting solid phase is the An(III) hydroxide:

\[
\text{An(OH)}_3(s) + 3\text{H}^+ \rightleftharpoons \text{An}^{3+} + 3\text{H}_2\text{O}
\]

with \( *K_{s.0}^c = [\text{An}^{3+}] \gamma_{\text{An}^{3+}} ([\text{H}^+] \gamma_{\text{H}^+})^{-3} (a_\text{w})^3 \)

At pH 5–13 in NaClO$_4$ and NaCl solutions, Am(III), Cm(III), and Pu(III) form only mononuclear hydrolysis species An(OH)$_n^{3-n}$ with \( n = 1–3 \), there is no indication for oligomers An$_m$(OH)$_n^{3m-n}$ [4–6]:

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An\(^{3+}\) + \(n\)H\(_2\)O ⇔ An(OH)\(_n\)\(^{3-n}\) + \(n\)H\(^+\)

with \(^*\beta_{1n}^{\circ} = [\text{An(OH)}_{n}^{3-n}] \gamma_{\text{An(OH)}_{n}^{3-n}} ([\text{H}^+] \gamma_{\text{H}^+})^n ([\text{An}^{3+}] \gamma_{\text{An}^{3+}})^{-1} (a_w)^{-n}\)

(2)

where \(^*\beta_{s,0}^{\circ}\) and \(^*\beta_{1n}^{\circ}\) are the equilibrium constants at zero ionic strength \((I = 0)\), \([i]\) is the concentration and \(\gamma_i\) the activity coefficient of species \(i\), and \(a_w\) is the activity of water. Activity coefficients may be calculated with the SIT as in the NEA-TDB reviews or with the Pitzer model. Since small differences in the ionic radii of aquo ions or complexes of equal charge and symmetry have only a slight effect on the activity coefficients, ion interaction coefficients (both SIT and Pitzer parameters) for Nd\(^{3+}\) and An\(^{3+}\) ions (An = Pu, Am, Cm) and their analogous aqueous complexes can be set equal [6,20–22].

### Solubility of Am(OH)\(_3\)(s) and aqueous speciation at high pH

There are numerous solubility studies with Am(III) hydroxides at pH 6–13 in carbonate-free NaClO\(_4\) and NaCl solutions [23–28]. Figure 1a shows experimental data determined after 1.5–2 nm ultrafiltration at \(I = 0.1\) M [23–26] or in dilute solutions [27]. The thermodynamic properties of the solid hydroxide and hence the solubility depends on the degree of crystallinity, i.e., on the particle/crystallite size which is affected by aging or ripening processes and by self-irradiation effects from the \(\alpha\)-activity of americium. The solubility calculated with the data selected in the NEA-TDB [6] for crystalline or aged Am(OH)\(_3\)(s) (\(\lg^*K_{s,0}^{\circ} = 15.6 \pm 0.6\)), amorphous Am(OH)\(_3\)(am) precipitates (\(\lg^*K_{s,0}^{\circ} = 16.9 \pm 0.8\)) and the complexes Am(OH)\(_{n}^{3-n}\) (\(\lg^*\beta_{1n}^{\circ} = -7.2 \pm 0.5, -15.1 \pm 0.7\) and \(-26.2 \pm 0.5\) for \(n = 1, 2,\) and 3, respectively) is represented by the lines in Fig. 1a. The use of the notation “crystalline” and “amorphous” to describe a solid phase and thereby its solubility is an oversimplification. The X-ray diffraction (XRD) data give only information of the bulk structure, while the solubility is determined by the surface characteristics or by fractions of smaller (“amorphous”) particles included in a bulk crystalline solid [6,7].

[Fig. 1](solubility.jpg) Solubility of Am(III) hydroxide at 25 °C. (a) Crystalline/aged Am(OH)\(_3\)(s) (solid line) and amorphous Am(OH)\(_3\)(s) (dashed line) at \(I = 0.1\) M (exp. data from [23–27]); (b) Aged Am(OH)\(_3\)(s) in 0–10 M KOH with additions of solid Ca(OH)\(_2\)(s) [29]. The SIT calculations are based on data selected in the NEA-TDB [6] and in this work for Am(OH)\(_4\)\(^–\) (see text).

The low americium concentrations at pH > 10, usually ascribed to the equilibrium between Am(OH)\(_3\)(s) and the neutral aqueous complex Am(OH)\(_3\)(aq), are rather scattered but at a constant level (\(\lg [\text{Am}] = -9.3 \pm 1.0\) for Am(OH)\(_3\)(am) and \(-10.6 \pm 0.8\) for aged or crystalline Am(OH)\(_3\)(s) [6]).

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Solubility studies in NaCl–NaOH, NaClO₄–NaOH, pure NaOH, or KOH solutions up to pH 14 show no indication for the formation of an anionic hydroxide complex \( \text{Am(OH)}_{4}^- \) that would increase the solubility at high pH [4,6]. In extremely alkaline solutions \(([\text{OH}^-] > 3 \text{ M})\), an increase of the americium concentration has been observed by Vitorge and Tran-The [29] who measured the solubility of fresh and aged \( \text{Am(III)} \) hydroxide precipitates in 0–10 M KOH with additions of solid \( \text{Ca(OH)}_2(s) \) to scavenge carbonate (Fig. 1b). Because of the high and variable ionic strength, these results were not evaluated and selected in the NEA-TDB reviews [4,6]. As shown in Fig. 1b, the solubility increase in 3–10 M KOH can be described with an equilibrium constant of \( \lg K^{\circ} = -0.5 \pm 0.4 \) for the reaction \( \text{Am(OH)}_3(aq) + \text{OH}^- \rightleftharpoons \text{Am(OH)}_4^- \) (corresponding to \( \lg \beta^{\circ} = -40.7 \pm 0.7 \)) and ion interaction (SIT) coefficients of \( \varepsilon[\text{Am(OH)}_3(aq), \text{K}^+/\text{OH}^-] = 0 \), \( \varepsilon[\text{OH}^-, \text{K}^+] = 0.09 \pm 0.01 \text{ kg mol}^{-1} \) [3–6] and \( \varepsilon[\text{Am(OH)}_4^-, \text{K}^+] = -0.03 \pm 0.05 \text{ kg mol}^{-1} \).

**Aqueous speciation by TRLFS with Cm(III)**

The sensitive TRLFS is often used to determine the aqueous speciation and complex formation constants of Cm(III) at trace concentration levels (c.f., Fanghanel and Kim [19]). In acidic chloride solutions up to 5 M NaCl and 2 M CaCl₂, the TRLFS emission band of the Cm³⁺(aq) ion with the maximum at \( \lambda_{\text{max}} = 593.8 \text{ nm} \) is not affected [30,31]. The formation of chloride complexes requires higher Cl⁻ concentrations; in 4 M CaCl₂ about 50% of the curium is present as CmCl²⁺ (\( \lambda_{\text{max}} = 594.9 \text{ nm} \)) and CmCl³⁺ (\( \lambda_{\text{max}} = 598.3 \text{ nm} \)) [30]. In TRLFS studies on the hydrolysis of Cm(III) in neutral and alkaline 0.1 M NaClO₄ [32] and dilute to concentrated NaCl [31], only the emission spectra of Cm(OH)²⁺ (\( \lambda_{\text{max}} = 598.8 \text{ nm} \)) and Cm(OH)³⁺ (\( \lambda_{\text{max}} = 603.5 \text{ nm} \)) were observed. Because of the low solubility at pH > 10, neither the complex Cm(OH)₂⁺(aq), which is expected to dominate the speciation at pH = 11–14, nor the complex Cm(OH)³⁻ could be detected. A TRLFS study of 10⁻⁸ M Cm(III) in 0.01–4.0 M NaOH showed no discernible fluorescence emission spectra and in 5.0–7.5 M NaOH only a weak, broad fluorescence band appeared between 600 and 625 nm [33]. The same observation was made in 5 M NaCl–NaOH with \([\text{OH}^-] = 1–4 \text{ M} \) [11]. Almost all of the curium is present as Cm₃⁺(OH)₃⁻(am), which shows no fluorescence (complete quenching) [33,34].

In alkaline CaCl₂ solutions, the chemical and spectroscopic behavior of Cm(III) is strikingly different. Rabung et al. [11] recorded TRLFS spectra in 0.1–3.5 M CaCl₂ at pH 11–12 and observed hitherto unknown Cm(III) emission bands caused by complexes with three, four, and six OH⁻ ligands. The emission bands of these complexes are regularly shifted to higher wavelength (\( \lambda_{\text{max}} = 607.5, 609.9, \) and 614.7 nm, respectively) compared to those of Cm³⁺(aq) (\( \lambda_{\text{max}} = 593.8 \text{ nm} \)), Cm(OH)²⁺ (\( \lambda_{\text{max}} = 598.8 \text{ nm} \)) and Cm(OH)³⁺ (\( \lambda_{\text{max}} = 603.5 \text{ nm} \)). These complexes, absent in NaCl–NaOH solutions, are stabilized by the association of Ca²⁺ ions, i.e., by the formation of ternary complexes Caₚ[Cm(OH)ₙ]³⁺²⁻ₙ [11].

**SOLUBILITY AND AQUEOUS SPECIATION OF NEODYMIUM AND CURIUM IN DILUTE TO CONCENTRATED NaCl, MgCl₂, AND CaCl₂ SOLUTIONS**

In order to derive a comprehensive thermodynamic model for the system M(III)–H⁺–Na⁺–Mg²⁺–Ca²⁺–Cl⁻–OH⁻–H₂O at 25 °C, valid over the entire range of ionic strength and pH, the solubility of Nd(III) hydroxide was determined under strict exclusion of CO₂(g) in 0.1, 0.5, 2.5, and 5.0 M NaCl (up to high OH⁻ concentrations of 0.1–4.0 M) and in 0.25, 1.0, 2.5, and 3.5 M MgCl₂ and CaCl₂ (up to maximum pHc, limited to values around 9 and 12, respectively, by the solubility of magnesium and calcium hydroxides or hydroxychlorides). The complementary information on the aqueous speciation, from the TRLFS studies mentioned above, is also taken into account. For calculations with the ion interaction model of Pitzer, the widely accepted data reported by Harvie et al. [2] are used for the matrix components. All calculations and equilibrium constants are given on the molal con-

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centration scale. Conversion factors to calculate $m_i$ [mol·(kg H₂O)⁻¹] from the molar concentrations $c_i$ [M = mol l⁻¹] are taken from [6].

Experimental

The solid Nd(III) hydroxide used in the present study was prepared under CO₂-free argon atmosphere by hydration of crystalline Nd₂O₃(cr) (Merck) in pure water (actinide and lanthanide oxides M₂O₃(cr) are not stable in aqueous solution and transform into the hydroxides [4,35,36]). The solid was stored for about three months under water. It clearly showed the known XRD pattern of Nd(OH)₃(cr) (JCPDS-File 70-0214). The experimental and analytical procedures and the chemicals used to prepare the matrix solutions were the same as in previous studies and described therein [10,11]. The samples for the solubility measurements were prepared and stored at 22 ± 2 °C in an Ar glove box. After equilibration times of 6–150 days and phase separation by either 10 kD ultrafiltration (pore size ca. 1.5 nm) or ultracentrifugation at 90 000 rpm (ca. 5 × 10⁵ g) the samples were analyzed for H⁺ and Nd concentrations. The latter were measured by inductively coupled plasma-mass spectroscopy (ICP-MS) (ELAN 6100 Perkin Elmer); detection limit: 10⁻¹⁰–10⁻⁹ M, depending on the concentration of the background electrolyte. The H⁺ concentrations in the NaCl, MgCl₂, and CaCl₂ solutions (molar scale: $pH_c = –\log c_{H^+}$; molal scale: $pH_m = –\log m_{H^+}$) were determined with combination pH electrodes (type ROSS, Orion) calibrated as described in detail in previous papers [1,10,11]. The H⁺ concentration in NaCl–NaOH solutions is calculated from the given OH⁻ concentration (for [OH⁻] > 0.01 M) and the conditional ion product of water.

XRD and scanning electron microscopy-energy-dispersive spectrometry (SEM-EDS) analysis at the end of the solubility experiments gave no indication for the transformation of the initial Nd(OH)₃(s) into a chloride-containing solid phase. The solubility-limiting solid is the same throughout the experiments in the dilute chloride media to 5.0 M NaCl and 3.5 M MgCl₂ and CaCl₂. This is further confirmed by the constant solubility after short and long equilibration times and by the consistent value of $lg^{*} K^\circ_{s,0} = 17.2 ± 0.4$ calculated for $I = 0$ from the H⁺ and Nd³⁺ concentrations and the well-known interaction coefficients of these ions [2,14,22]. However, this was not the case in an additional study in 4.5 M MgCl₂ where SEM-EDS and the significantly diminished XRD pattern of Nd(OH)₃(cr) indicated the transformation into an amorphous Nd(OH)₃–xClₓ(s) phase with lower solubility. These results are not further discussed.

Solubility of Nd(OH)₃(s): Comparison with literature data

In a review of the earlier literature on the solubility and hydrolysis of the lanthanides, Baes and Mesmer [15] recommended a solubility constant of $lg^{*} K^\circ_{s,0} = 18.6$ for Nd(OH)₃(s) and hydrolysis constants of $lg^{*} \beta_{11}^{\circ}(Nd(OH)_{3-n}) = –8.0$, $–16.9$, $–26.5$, and $–37.1$ for $n = 1–4$ and $lg^{*} \beta_{22}^{\circ}(Nd_2(OH)_4^{4+}) = –13.86$ (speciation calculations with this constant from potentiometric titration show that the dimer is not relevant at solubility equilibrium conditions). The value of $lg^{*} \beta_{11}^{\circ} = –8.0$ appears too small compared to mean values for Eu(III), $lg^{*} \beta_{11}^{\circ} = –7.5 ± 0.4$ [37] and $–7.64 ± 0.04$ [38], or $lg^{*} \beta_{11}^{\circ} = –7.2 ± 0.5$ for Am(III) and Cm(III) [6]. The data for Eu(III), Am(III), and Cm(III) are based on a much larger number of experimental studies and methods. The hydrolysis constants for $n = 2$ and 3 are interpolated from $lg^{*} \beta_{22}^{\circ} = –8.0$ and $lg^{*} \beta_{11}^{\circ} = –37.1$, but the equilibrium constant for the tetrahydroxide complex is overestimated by several orders of magnitude. The value of $lg K^\circ_{3–4} = 3.4$ derived by Baes and Mesmer [15] from solubility data for Nd(OH)₃(s) in NaOH solutions must be due to analytical problems or experimental shortcomings in the underlying solubility studies [39,40] which report concentrations of 10⁻⁵ to 10⁻⁴ M in the range of the solubility minimum to high pH. Neither the solubility of Am(OH)₃(s) (Fig. 1), with $lg K^\circ_{3–4} = –0.5$, nor our results for Nd(OH)₃(s) (Fig. 2) show an indication for a solubility increase up to pH 14. The solubility curves of Nd(OH)₃(s) and Am(OH)₃(s) in 0.1 M
NaCl or NaClO₄ (Figs. 1a and 2a) and in 5.0 M NaCl (Fig. 2b), show the same dependence on pH, just shifted in parallel by about 1.5 lg-units. For these reasons, it is more convenient to use the Am(III)/Cm(III) data as analogs for Nd(III), or the slightly different values of lg°β₁₁ = –7.4 ± 0.4 and lg°β₁₂ = –15.7 ± 0.7 derived from our solubility study with Nd(OH)₃(s).

In later reviews of thermodynamic data for the solid lanthanide hydroxides, Diakonov et al. [35,36] pointed out that the solubility constant lg°K°,₀ = 18.6 recommended by Baes and Mesmer [15] refers to highly soluble amorphous precipitates. From their compilation of published data, they calculated mean values of lg°K°,₀ = 18.66 ± 0.55 for fresh, amorphous precipitates of Nd(OH)₃(s) and 16.02 ± 0.37 for aged and crystalline Nd(OH)₃(s) [35,36]. The solubility constant of the Nd(OH)₃(s) phase used in the present work (lg°K°,₀ = 17.2 ± 0.4) lies between these values. Figure 2a shows our results in 0.1 M NaCl in comparison with the solubility calculated with the equilibrium constants proposed by Baes and Mesmer [15] (dashed line) and the data reported by Silva [23] and Rao et al. [41] for Nd(OH)₃(cr) at 25 °C in 0.1 M NaClO₄ and 0.1 M NaCl, respectively. The latter authors prepared well-crystalline Nd(III) hydroxide phases in 5 M NaOH at 90 °C. The solubility determined in this solid at pH 6–8, is in the range of the data for crystalline/aged Am(OH)₃(s) (lg°K°,₀ = 15.6 ± 0.6) and 1–2 lg-units lower than the data obtained for Nd(OH)₃(s) in the present work. This may be explained by a difference in particle/crystallite size. The present results correspond to a less-crystalline solid phase consisting of smaller particles. However, the solubility data determined by Silva [23] and Rao et al. [41] at pH 8.5–9.5 approach our results, indicating that these values refer to smaller particles included in their bulk crystalline solid (comparable to the particle size of the Nd(OH)₃(s) solid used in our study). Similar particle size effects are known for hydrous Th(IV) oxides and discussed in length in [7].

**Solubility of Nd(OH)₃(s) and Cm(III)–TRLFS in NaCl and NaCl–NaOH solutions**

The experimental solubility data for Nd(OH)₃(s) in 0.1, 0.5, 2.5, and 5.0 M NaCl (Fig. 3) can be described with the simple speciation scheme known for trivalent actinides, i.e., with Nd³⁺ and mono-nuclear hydrolysis species Nd(OH)ₙ³⁻ⁿ (n = 1, 2, and 3). The large scatter of the data at pH_m > 9 is an indication that the measured concentrations are affected by small (1–2 nm) polymers. On the one hand, uncharged species like Nd(OH)₃(aq) and Nd₃(OH)₃n(aq) have a high tendency toward sorption on the
vessel walls or filter surface, on the other hand, incomplete removal of small polymers by ultrafiltration or ultracentrifugation may lead to increased total Nd concentrations. However, even up to high \( \text{OH}^- \) concentrations in 5 M NaCl–NaOH, there is no indication for a solubility increase due to the formation of anionic hydroxide complexes. This is consistent with the equilibrium constant derived above for Am\((\text{OH})_4^-\) from the solubility of Am\((\text{OH})_2(s)\) in 0–10 M KOH [29] (c.f., dashed concentration lines calculated for Nd\((\text{OH})_4^-\)). It is also consistent with the observation that TRLFS shows no discernible Cm(III) emission spectrum at \([\text{OH}^-] = 1–4 \text{ M}\) in 5 M NaCl–NaOH [11]. The curium concentrations measured after 10 kD ultrafiltration, \(\lg [\text{Cm}] = -8.3 \pm 0.1\) (c.f., squares in Fig. 3), should be sufficient for a clear TRLFS emission spectrum, but obviously the dissolved curium is almost completely present as Cm\(_m\)(OH)\(_3\) polymers which show no fluorescence emission bands [33,34].

**Solubility of Nd\((\text{OH})_3(s)\) and Cm(III)–TRLFS in MgCl\(_2\) and alkaline CaCl\(_2\) solutions**

The results of the solubility experiments in 0.25, 1.0, 2.5, and 3.5 M MgCl\(_2\) (\(pH_m < 9\)) and CaCl\(_2\) (\(pH_m < 12\)) are shown in Fig. 4. In the overlapping \(pH_m\) regions the solubilities in equimolar MgCl\(_2\) and alkaline CaCl\(_2\) solutions are shown as squares with cross inside.

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**Fig. 3** Solubility of Nd\((\text{OH})_3(s)\) in 0.1, 0.5, 2.5, and 5.0 M NaCl (\(m_{\text{NaCl}} = 0.10, 0.51, 2.64, 5.61 \text{ mol kg}^{-1}\)); experimental data (molal scale) and Pitzer model calculation (thick lines: total Nd concentrations, thin lines: contributions of the different species). The aqueous Cm(III) concentrations determined after ultrafiltration in 5.0 M NaCl–NaOH solutions are shown as squares with cross inside.
and CaCl$_2$ solutions are identical or close to each other. (Note that Fig. 4 shows molal values of lg ([Nd]/mol kg$^{-1}$) plotted vs. pH$_{m} = – \lg ([H^+]$/mol kg$^{-1}$), and that the conversion factors from molarity to molality and also lg $\gamma_{H^+}$ in eqs. 1 and 2 diverge to a certain extent with increasing electrolyte concentration, either 0.25, 1.02, 2.67, and 3.86 mol kg$^{-1}$, $m_{MgCl_2} = 0.25, 1.02, 2.67$, and $3.86$ m MgCl$_2$ or 0.25, 1.02, 2.68, and 3.91 mol kg$^{-1}$; experimental data (molal scale) and Pitzer model calculation (fat lines: total Nd concentrations, thin lines: contributions of the different species). The Cm(III) concentrations determined after ultrafiltration in the TRLFS samples are shown as squares with cross inside.

Fig. 4 Solubility of Nd(OH)$_3$(s) in 0.25, 1.0, 2.5, and 3.5 M MgCl$_2$ and CaCl$_2$ ($m_{MgCl_2} = 0.25, 1.02, 2.67,$ and 3.86 mol kg$^{-1}$, $m_{CaCl_2} = 0.25, 1.02, 2.68,$ and 3.91 mol kg$^{-1}$); experimental data (molal scale) and Pitzer model calculation (fat lines: total Nd concentrations, thin lines: contributions of the different species). The Cm(III) concentrations determined after ultrafiltration in the TRLFS samples are shown as squares with cross inside.

and CaCl$_2$ solutions are identical or close to each other. (Note that Fig. 4 shows molal values of lg ([Nd]/mol kg$^{-1}$) plotted vs. pH$_{m} = – \lg ([H^+]$/mol kg$^{-1}$), and that the conversion factors from molarity to molality and also lg $\gamma_{H^+}$ in eqs. 1 and 2 diverge to a certain extent with increasing electrolyte concentration, either 0.25, 1.02, 2.67, and 3.86 m MgCl$_2$ or 0.25, 1.02, 2.68, 3.91 m CaCl$_2$). Contrary to the solubility at high pH in NaCl solutions, the solubility of Nd(OH)$_3$(s) in 1.0, 2.5, and 3.5 M CaCl$_2$ clearly increases in the range pH$_{m} = 11–12$. The higher the CaCl$_2$ concentrations the more pronounced is this effect. Another noteworthy difference compared to the results in alkaline NaCl media is the fact that the data in alkaline CaCl$_2$ solutions are much less scattered, indicating that the measured Nd concentrations are caused by well-defined ionic species.

These observations and conclusions are confirmed by TRLFS emission spectra with $[Cm]_{tot} = 2 \times 10^{-7}$ M in 0.1–3.5 M CaCl$_2$ at pH$_{m} = 11.7$ and in three sets at constant ionic strength (1.0, 2.5, and 3.5 M CaCl$_2$) and varying pH$_{m}$ [11] (Fig. 5). Peak deconvolution and the evaluation of the pH dependence of the spectroscopic data showed that Cm(III) complexes with three, four, and six OH$^-$ ligands are formed ($\lambda_{\text{max}} = 607.5, 609.9$, and 614.7 nm, respectively). As these species are absent in NaCl–NaOH media, although the Cm(III) concentrations after 10 kD ultrafiltration are similar to those
in 1.0 M CaCl₂ (about 10⁻⁸ M), they must be stabilized by the association of Ca²⁺ ions. This also explains the strong increase of the intensity of the emission bands in 0.1–1.0 M CaCl₂ (Fig. 5a) which are caused by the tri- and tetrahydroxide complexes Caₓ[Cm(OH)₃]₂ and Caₓ[Cm(OH)₄]₂⁻. The hexa-hydroxide complex Ca₀[Cm(OH)₆]²⁻ dominates at higher CaCl₂ concentrations and pHₘ > 11.5. The spectroscopic speciation is supported by the Cm(III) concentrations determined after 10 kD ultrafiltration of the TRLFS samples in 1.0, 2.5, and 3.5 M CaCl₂ (c.f., squares in Fig. 4). These concentrations, [Cm(III)]_aq in equilibrium with colloidal Cm(OH)₃(am), clearly increase from pHₘ 10.5 to 12 and also with increasing CaCl₂ concentration. At pHₘ > 11.5 in 3.5 M CaCl₂, the curium ([Cm]ₜₒₜ = 2 × 10⁻⁷ M) is completely dissolved as ionic species. It may be accidental that these Cm(III) concentrations coincide with the solubility data for Nd(OH)₃(s), i.e., that the solubility constant of small colloidal Cm(OH)₃(am) particles is equal to that of our Nd(OH)₃(s) phase. However, the finding that the dependence on the CaCl₂ concentration and pH is the same for Cm(III) and Nd(III) is not unexpected as it confirms the usual (qualitative and quantitative) analogy for the aqueous complexes of Cm³⁺ and Nd³⁺.

The extremely different chemical and spectroscopic behavior of Cm(III) in alkaline CaCl₂ solutions compared to that in pure NaOH and NaCl–NaOH solutions and the analogous discrepancies for the solubility of Nd(OH)₃(s) in these media cannot be explained by binary hydroxide complexes M(OH)ₙ³⁻ and different ion interaction coefficients with Ca²⁺ compared to those with Na⁺. A thermodynamic model valid for both Ca-free and -containing solutions requires the formulation as ternary complexes Caₚ[M(OH)ₙ]²⁺ₚ⁻ₙ. The number of associated Ca²⁺ ions cannot be determined independently with the presently available methods. However, in analogy to the M(IV) complexes Caₙ[Zr(OH)₆]¹⁴⁺ and Caₙ[Th(OH)₈]³⁺, where the number of Ca²⁺ ions in the second shell and the coordination structure could be determined by EXAFS [9] (one Ca²⁺ ion bound to two OH⁻ ligands via edges of the [M(OH)ₙ⁻] coordination polyhedra), it appears reasonable to assume the stoichiometries Caₙ[Cm(OH)₃]²⁺, Ca₂[Cm(OH)₄]³⁺, and Ca₃[Cm(OH)₆]₃⁺. In our recent study [11], the SIT was used to calculate the formation constants lg*β°ᵣ,p,l,n and ion interaction coefficients for these ternary complexes from the spectroscopic data for Cm(III) in 1.0, 2.5, and 3.5 M CaCl₂ and the solubility constant for colloidal Cm(OH)₃(am) which is equal to that of Nd(OH)₃(s):
\[ p\text{Ca}^{2+} + \text{Cm}^{3+} + n\text{H}_2\text{O} \Leftrightarrow \text{Ca}_p[\text{Cm(OH)}_n]^{2p+3-n} + n\text{H}^+ \]

\[ \lg*\beta_{1,1,3}^p = -26.3 \pm 0.5, \quad \varepsilon(\text{Ca}[\text{Cm(OH)}_3^{2+}, \text{Cl}^-]) = 0.05 \pm 0.04 \text{ kg mol}^{-1} \]

\[ \lg*\beta_{2,1,4}^p = -37.2 \pm 0.6, \quad \varepsilon(\text{Ca}_2[\text{Cm(OH)}_4^{3+}, \text{Cl}^-]) = 0.29 \pm 0.07 \text{ kg mol}^{-1} \]

\[ \lg*\beta_{3,1,6}^p = -60.7 \pm 0.5, \quad \varepsilon(\text{Ca}_3[\text{Cm(OH)}_6^{3+}, \text{Cl}^-]) = 0.00 \pm 0.06 \text{ kg mol}^{-1} \]

The SIT coefficients for the other ions involved are given in the NEA-TDB [3–6]: \( \varepsilon(M^{3+}, \text{Cl}^-) = 0.23 \pm 0.02 \) for \( M = \text{Nd}, \text{Cm}, \) and \( \text{Am}, \varepsilon(\text{Ca}^{2+}, \text{Cl}^-) = 0.14 \pm 0.01 \) and \( \varepsilon(\text{H}^+, \text{Cl}^-) = 0.12 \pm 0.01 \text{ kg mol}^{-1} \).

In the present study, the TRLFS results are re-evaluated with the Pitzer equations. As \( \lg*\beta_{1,1,3}^p \) values at only three different ionic strengths do not allow a reasonable fit of all parameters, the constants at \( I = 0 \) derived with the SIT are used as fixed values. Following a recommendation to keep consistency between SIT and Pitzer model [20], the Pitzer parameters \( \beta^{(1)}(\text{Ca}_p[\text{Cm(OH)}_n]^{2p+3-n}, \text{Cl}^-) \) for the charge types 2:1 and 3:1 are fixed at 1.6 and 4.3 kg mol \(^{-1} \), respectively. Including the data for these ternary complexes in a comprehensive thermodynamic model (c.f., discussion below in the final section) allows the geochemical modeling of the solubility and hydrolysis of trivalent actinides and Nd(III) over the entire pH range in dilute to concentrated NaCl, MgCl\(_2\), and CaCl\(_2\) media at 25 °C. This is illustrated in Figs. 3 and 4, where the total solubility of Nd(OH)\(_3\)(s) and the different species contributions calculated with the Pitzer approach are shown as fat and thin lines, respectively. Corresponding calculations with the SIT are practically identical for \( I \leq 3 \text{ mol kg}^{-1} \), even at high ionic strength they deviate less than 0.5 lg-units from the Pitzer model calculations.

**Thermodynamic model for solid hydroxides and aqueous complexes of trivalent actinides and Nd(III) in the system M(III)–H\(^+\)–Na\(^+\)–Mg\(^{2+}\)–Ca\(^{2+}\)–Cl\(^–\)–OH\(^–\)–H\(_2\)O (25 °C)**

The standard-state equilibrium constants \( (I = 0, 25 °C) \) for solid hydroxides and aqueous Am(III)/Cm(III) and Nd(III) complexes in NaCl, MgCl\(_2\), and CaCl\(_2\) solutions are summarized in Table 1; ion interaction coefficients for the aqueous species are listed in Tables 2 and 3. The Pitzer parameters (Table 2) refer to auxiliary data reported by Harvie et al. [2] for the seawater salt system, SIT coefficients for the ions of the matrix components are taken from the NEA-TDB [3–6]. The ion interaction parameters for Nd\(^{3+}\) ions (equal to those for An\(^{3+}\) ions [6,21,22]) are well known from data in binary NdCl\(_3\) and ternary NdCl\(_3–NaCl\) and NdCl\(_3–CaCl_2\) systems [14,22]. The equilibrium constants and Pitzer parameters for chloride complexes are based on TRLFS data for Cm(III) [22,30].

The thermodynamic data selected in the NEA-TDB [6] for solid Am(III) hydroxides and the hydrolysis constants \( \lg*\beta_{1,1,n}^p (n = 1–3) \) for Am(III)/Cm(III) are well ascertained. The solubility constant of the aged Nd(OH)\(_3\)(s) phase used in the present study, \( \lg*K_{s,0}^p = 17.2 \pm 0.4 \), and the value of 16.0 ± 0.4 proposed by Diakonov et al. [35,36] for aged and crystalline Nd(OH)\(_3\)(s) are close to the values selected in the NEA-TDB [6] for amorphous and aged/crystalline Am(OH)\(_3\)(s). The very high values of \( \lg*K_{s,0}\text{[Nd(OH)}_3\text{(am)]} = 18.66 \pm 0.55 \) [35,36] or 18.6 [15] are probably not appropriate for long-term model calculations. The hydrolysis constants \( \lg*\beta_{11}^p = -7.4 \pm 0.4 \) and \( \lg*\beta_{12}^p = -15.7 \pm 0.7 \) derived from our solubility study with Nd(OH)\(_3\)(s) are in the range of the values selected in the NEA-TDB [6] from numerous studies and different experimental methods for Am(III) and Cm(III). The previously reported SIT coefficients [6] and particularly the Pitzer parameters [18,22] for M(OH)\(_2^+/\text{Cl}^-\) and M(OH)\(_2^+/\text{Cl}^-\) are mainly based on a TRLFS study in 0–6 m NaCl [31]. Their application to MgCl\(_2\) and CaCl\(_2\) solutions of higher ionic strength considerably overpredicts the formation of the dihydroxide complex M(OH)\(_2^+/\) and hence the solubility in the range \( pH_m = 8–11 \). The Pitzer parameters for these species have therefore been adjusted to the present solubility data for Nd(OH)\(_3\)(s) and literature data for the solubility of aged Am(OH)\(_3\)(s) in 0.1, 0.6, and 5.0 M NaCl [26,28]. Ternary parameters for cationic M(III) species in MgCl\(_2\) solutions are set equal to the corresponding parameters with Ca\(^{2+}\). The SIT coefficient for the monohydroxide complex,
ε[M(OH)\textsuperscript{2+}, Cl\textsuperscript{−}] = −0.04 ± 0.07 kg mol\textsuperscript{−1} [6] can be retained, but the value of ε[M(OH)\textsuperscript{2+}, Cl\textsuperscript{−}] has to be revised, from −0.27 ± 0.20 [6] into −0.06 ± 0.08 kg mol\textsuperscript{−1}.

**Table 1** Equilibrium constants (I = 0, 25 °C) for the solid hydroxides and aqueous complexes of Am(III)/Cm(III) and Nd(III).

<table>
<thead>
<tr>
<th>Solubility: (\lg^\circ K_{\text{s0}}) [M(OH)\textsubscript{3}(s) + 3H\textsuperscript{+} ⇔ M\textsuperscript{3+} + 3H\textsubscript{2}O]</th>
<th>Am(OH)\textsubscript{3}(cr/aged)</th>
<th>15.6 ± 0.6 [6]</th>
<th>Nd(OH)\textsubscript{3}(cr/aged)</th>
<th>16.0 ± 0.4 [35]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am(OH)\textsubscript{3}(am):</td>
<td>16.9 ± 0.8 [6]</td>
<td>Nd(OH)\textsubscript{3}(s):</td>
<td>17.2 ± 0.4 p.w.</td>
<td></td>
</tr>
</tbody>
</table>

Chloride complexes: \(\lg^\circ \beta_{n}^\circ\) [M\textsuperscript{3+} + nCl\textsuperscript{−} ⇔ MCl\textsubscript{n}\textsuperscript{3−n}]

| \(\text{AnCl}_2^+\) (Am/Cm) | 0.24 ± 0.03 [6,22] | \(\text{NdCl}_2^+\): analogous Cm value |
| \(\text{AnCl}_2\) (Am/Cm): | −0.74 ± 0.05 [6,22] | \(\text{NdCl}_2^+\): analogous Cm value |

Hydroxide complexes: \(\lg^\circ \lambda_{i}^\circ\) [M\textsuperscript{3+} + nH\textsubscript{2}O ⇔ M(OH)\textsubscript{n}\textsuperscript{3−n} + nH\textsuperscript{+}]

| \(\text{An(OH)}\textsubscript{2+}\) (Am/Cm) | −7.2 ± 0.5 [6] | \(\text{Nd(OH)}\textsubscript{2+}\): analogous Am value |
| \(\text{An(OH)}\textsubscript{2}\) (Am/Cm): | −15.1 ± 0.7 [6] | \(\text{Nd(OH)}\textsubscript{2}\): analogous Am value |

| \(\text{An(OH)}\textsubscript{3}(aq)\) | −26.2 ± 0.5 [6] | \(\text{Nd(OH)}\textsubscript{3}(aq): analogous Am value |
| \(\text{An(OH)}\textsubscript{3}\) (Am/Cm): | −40.7 ± 0.7 p.w. | \(\text{Nd(OH)}\textsubscript{3}: analogous Am value |

| \(\text{Ca}[\text{M(OH)}\textsubscript{3}]\textsubscript{2+}\) | −26.3 ± 0.5 [11], p.w. | \(\text{Ca}[\text{Nd(OH)}\textsubscript{3}]\textsubscript{2+}: analogous Cm value |
| \(\text{Ca}_2[\text{M(OH)}\textsubscript{4}]\textsubscript{3+}\) | −37.2 ± 0.6 [11], p.w. | \(\text{Ca}_2[\text{Nd(OH)}\textsubscript{4}]\textsubscript{3+}: analogous Cm value |
| \(\text{Ca}_3[\text{M(OH)}\textsubscript{6}]\textsubscript{3+}\) | −60.7 ± 0.5 [11], p.w. | \(\text{Ca}_3[\text{Nd(OH)}\textsubscript{6}]\textsubscript{3+}: analogous Cm value |

Table 2 Ion interaction (Pitzer) coefficients for M(III) species (M = Am, Cm, Pu, and Nd) in chloride media at 25 °C; \(\beta_{ik}^{(0)}\), \(\beta_{ik}^{(1)}\), \(\lambda_{ik}\), and \(\theta_{ij}\) in [kg mol\textsuperscript{−1}], \(C_{ik}^\theta\) and \(\psi_{ijk}\) in [kg\textsuperscript{2} mol\textsuperscript{−2}].

| Binary Pitzer parameters | Ternary Pitzer parameters |
|---|---|---|---|---|---|---|---|
| i | k | \(\beta_{ik}^{(0)}\) | \(\beta_{ik}^{(1)}\) | \(C_{ik}^\theta\) | j | \(\theta_{ij}\) | \(\psi_{ijk}\) | Ref. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.5856 | 5.60 | −0.016 | Na\textsuperscript{+} | 0.10 | 0 | [22] |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.593 | 3.15 | −0.006 | Na\textsuperscript{+} | 0 | 0 | [22] |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.516 | 1.75 | 0.010 | Na\textsuperscript{+} | 0 | 0 | [22] |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.055 | 1.81 | 0 | Na\textsuperscript{+} | 0 | 0 | [18] |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | −0.13 | 0 | 0 | Na\textsuperscript{+} | 0 | 0 | p.w. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0 | 0 | 0 | Na\textsuperscript{+} | 0 | 0 | p.w. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0 | 0 | 0 | Cl\textsuperscript{−}/OH\textsuperscript{−} | 0 | 0 | p.w. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.21 | 1.6\textsuperscript{a} | 0 | Ca\textsuperscript{2+}/Mg\textsuperscript{2+} | 0 | 0 | p.w. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.70 | 4.3\textsuperscript{a} | 0 | Ca\textsuperscript{2+}/Mg\textsuperscript{2+} | 0 | 0 | p.w. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0.37 | 4.3\textsuperscript{a} | 0 | Ca\textsuperscript{2+}/Mg\textsuperscript{2+} | 0 | 0 | p.w. |
| M\textsuperscript{3+} | Cl\textsuperscript{−} | 0 | 0 | 0 | Na\textsuperscript{+} | −0.2 | \(\lambda_{ik} = −0.2\) | [22] |

\(\text{Ca}[\text{M(OH)}\textsubscript{3}]\textsubscript{2+}\) | −0.2 | \(\lambda_{ik} = 0\) for \(k = \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Cl}^−, \text{OH}^−\) | [22] |
| \(\text{Ca}[\text{M(OH)}\textsubscript{3}]\textsubscript{2+}\) | −0.2 | \(\lambda_{ik} = 0\) for \(k = \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Cl}^−, \text{OH}^−\) | [22] |

\textsuperscript{a}Fixed value for the corresponding charge type, according to [20].

\textsuperscript{b}Strong interaction with Ca\textsuperscript{2+} must be expressed in terms of Ca–M(III)–OH complex formation, interaction with Mg\textsuperscript{2+} is not relevant (pH\textsubscript{m} < 9 in MgCl\textsubscript{2} solutions).
Table 3 Irron interaction (SIT) coefficients $\epsilon_{ik}$ [kg mol$^{-1}$] for M(III) species (M = Am, Cm, Pu, and Nd) in chloride media at 25 °C.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$k$</th>
<th>$\epsilon_{ik}$ [kg mol$^{-1}$]</th>
<th>$i$</th>
<th>$k$</th>
<th>$\epsilon_{ik}$ [kg mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{M}^{3+}$</td>
<td>$\text{Cl}^-$</td>
<td>0.23 ± 0.02 [6]</td>
<td>$\text{M(OH)}_2^+$</td>
<td>$\text{Cl}^-$</td>
<td>-0.04 ± 0.07 [6]</td>
</tr>
<tr>
<td>$\text{M(OH)}_2^+$</td>
<td>$\text{Cl}^-$</td>
<td>-0.06 ± 0.08 p.w.</td>
<td>$\text{M(OH)}_2^+$</td>
<td>$\text{Na}^+$</td>
<td>-0.17 ± 0.10 p.w.</td>
</tr>
<tr>
<td>$\text{Ca}[\text{M(OH)}_3]^{2+}$</td>
<td>$\text{Cl}^-$</td>
<td>0.05 ± 0.04 [11]</td>
<td>$\text{M(OH)}_3^+$</td>
<td>$\text{K}^+$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Ca}_2[\text{M(OH)}_4]^3+$</td>
<td>$\text{Cl}^-$</td>
<td>0.29 ± 0.07 [11]</td>
<td>$\text{M(OH)}_4^-$</td>
<td>$\text{K}^+$</td>
<td>-0.03 ± 0.05 p.w.</td>
</tr>
</tbody>
</table>

$^a$Strong interaction with Ca$^{2+}$ must be expressed in terms of Ca–M(III)–OH complex formation, interaction with Mg$^{2+}$ is not relevant because pH$_m$ < 9 in MgCl$_2$ solutions.

The NEA-TDB value of $\log^{\beta}_13[\text{Am(OH)}_3(aq)] = -26.2 \pm 0.5$ [6], exclusively based on solubility data for Am(OH)$_3$(s) in alkaline solutions of low ionic strength, is adopted in the present work for Nd(OH)$_3$(aq). The somewhat increased solubility of Am(OH)$_3$(s) and Nd(OH)$_2$(s) at pH 10–14 in 5.0 M NaCl compared to lower ionic strength (c.f., Figs. 2 and 3) may be described (for practical purposes) by introducing an interaction coefficient for the neutral M(OH)$_3$(aq) complex, e.g., a Pitzer coefficient of $\lambda(\text{M(OH)}_3(aq), \text{Na}^+)$ = $-0.2$ kg mol$^{-1}$ [22] (Table 2), corresponding to a SIT coefficient of $\epsilon(\text{M(OH)}_3(aq), \text{Na}^+) = -0.17$ kg mol$^{-1}$ (Table 3). However, the large scatter of the measured Am or Nd concentrations and the absence of a Cm(III) emission band in alkaline NaCl solutions indicate that these concentrations are rather caused by small polymers than by the mononuclear complex M(OH)$_3$(aq).

The formation constant for the tetrahydroxide complex is derived in the present work from the solubility increase of aged Am(OH)$_3$(s) in 0–10 M KOH [29] (Fig. 1b). This effect is well described with $\log^{\beta}_14 = -40.7 \pm 0.7$ and $\epsilon(\text{Am(OH)}_4^-, \text{K}^+)$ = $-0.03 \pm 0.05$ kg mol$^{-1}$ or equivalently with the Pitzer model and all parameters for the interactions of Am(OH)$_2$(aq) and Am(OH)$_3^-$ with K$^+$ and/or OH$^-$ equal to zero. However, the KOH matrix solutions used in [29] were saturated with Ca(OH)$_2$(s) and contained small but definite Ca$^{2+}$ concentrations—vice versa than in alkaline CaCl$_2$ solutions with rather high Ca$^{2+}$ but low OH$^-$ concentrations (pH$_m$ < 12) where the solubility increase of Nd(OH)$_3$(s) is consistently described with the data derived for Ca[Ca(OH)$_3$]$_2^{2+}$, Ca$_2$[Ca(OH)$_4$]$_3^{3+}$, and Ca$_3$[Ca(OH)$_6$]$_3^{3+}$ from the TRLFS study with Cm(III). It cannot be excluded that the solubility increase of Am(OH)$_3$(s) in 3–10 M KOH might also be caused by ternary Ca–Am(III)–OH complexes, but a fit including species like Ca[Am(OH)$_3$]$_2^{2+}$ or Ca[Am(OH)$_4$]$_4^{3+}$ and Pitzer parameters for their interactions with OH$^-$ and K$^+$ would be highly speculative.

Equilibrium constants for Pu(III) are much less ascertained than for Am(III) or Cm(III). The solubility constant determined by Felmy et al. [21] for fresh precipitates of Pu(OH)$_3$(s), $\log^{\beta}_{14}(\text{Pu(OH)}_2^+) = -6.9 \pm 0.3$ [5,6], unknown data for other Pu(III) complexes must be adopted from the Am(III)/Cm(III) analogs. This approach was successfully applied to plutonium solubilities under reducing conditions in MgCl$_2$ and CaCl$_2$ solutions in contact with iron powder [12].

REFERENCES


