



# Study of barium and radium complex formation with EDTA in alkaline sodium chloride media

Master's thesis in the Nuclear Science and Technology programme

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## MASTER'S THESIS

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Cover: The apparent stability constants of the RaEDTA<sup>2-</sup> complex formation extrapolated to zero ionic strength using the specific ion interaction theory

Study of barium and radium complex formation with EDTA in alkaline sodium chloride media

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#### Abstract

The complex formation of  $Ra^{2+}$  and  $Ba^{2+}$  with ethylenediaminetetraacetic acid (EDTA) was studied at two pH regions where the EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> species are dominant. The complex formation was investigated at 25°C in NaCl ionic media at ionic strengths 0.2, 0.5, 1.0, 2.0 and 2.5 mol·l<sup>-1</sup>, using an ion exchange method and batch technique. Radium-226 and barium-133 were used as radiotracers and their activities in the aqueous phases were measured using gamma spectrometry and liquid scintillation counting, respectively. The specific ion interaction theory, SIT, was used to account for the complex formation between the ionic media and the ligand, [NaEDTA]<sup>3-</sup> and [NaHEDTA]<sup>2-</sup> complex formations, as well as for extrapolating determined apparent stability constants to zero ionic strength (BaEDTA<sup>2-</sup>:  $log_{10}\beta=9.88\pm0.11$ and RaEDTA<sup>2-</sup>:  $\log_{10}\beta = 9.11 \pm 0.09$ ). SIT was also used in order to obtain the Ba<sup>2+</sup> and Ra<sup>2+</sup> ion interaction coefficient terms ( $\Delta\epsilon(BaEDTA^{2-})=-(0.44\pm0.07)$ ;  $\Delta\epsilon(RaEDTA^{2-})=-(0.54\pm0.06)$ ). From these terms, the ion interaction coefficients of Ba2+ and Ra2+ with various ions were calculated as: e(Na+,BaEDTA2-)=- $(0.03\pm0.11)$  and  $\varepsilon(Na^+, RaEDTA^{2-}) = -(0.10\pm0.11)$ . It was found that in the HEDTA<sup>3-</sup> dominant pH region, the reaction of  $Ba^{2+}$  and  $Ra^{2+}$  with the HEDTA<sup>3-</sup> results in the emission of a proton and formation of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes. The comparison of ion interaction parameters of Ba<sup>2+</sup> and Ra<sup>2+</sup> strongly indicate that both metal ions and their EDTA complexes have similar activity coefficients and undergo similar short-range interactions in aqueous NaCl media.

Keywords: alkaline earth metal, EDTA, radium, complex formation, activity coefficient, SIT, specific ion interaction theory, infinite dilution, ionic strength, barium

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## 1. Introduction

Radium is the heaviest element in the alkaline earth metal group, with 34 known isotopes [KAR15]. Only four isotopes are found naturally,  $^{226}$ Ra (t<sub>1/2</sub>=1600 y),  $^{228}$ Ra (t<sub>1/2</sub>=5.75 y),  $^{223}$ Ra (t<sub>1/2</sub>=11.43 d), and  $^{224}$ Ra  $(t_{1/2}=3.66 \text{ d})$ , as only these are part of the naturally occurring <sup>238</sup>U, <sup>235</sup>U and <sup>232</sup>Th decay-series. Uranium and thorium are abundant in many different rock and mineral types, which makes radium globally widespread [LEE05]. Radium can be transferred from rocks to water by several mechanisms: diffusion, alpha recoil, leaching and ion exchange, where the ion exchange is the most probable environmental mechanism causing relatively high radium concentrations [LEE05b]. The Ra<sup>2+</sup> ion is replaced most efficiently by other alkaline earth metal ions,  $Ca^{2+}$ ,  $Ba^{2+}$  and  $Sr^{2+}$ , but can also be replaced to some extent by alkali metal ions, mainly Na<sup>+</sup> and K<sup>+</sup> [LEE05b]. Radium is therefore one of the most abundant naturally occurring radioactive materials (NORM) in saline waters, in which it is present in its cation form, Ra<sup>2+</sup>. There are different mechanisms of radium accumulation in the waste streams, but its co-precipitation with similar-size ions (e.g. Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>) in the form of carbonates and sulfates [LEE05b] is one of the main mechanisms. The radium isotopes are of significant environmental concern, and its isotopes may pose a health risk because of their presence in soils and drinking water [COT90]. <sup>226</sup>Ra is of particular concern as it has a half-life of 1600 years, and is one of the most radiotoxic alpha emitters present in the environment [EIS90]. Isolation and removal of Ra<sup>2+</sup> from these waste streams can be done through dissolution using chelating agents such as EDTA or ion exchange [LEE05b].

The radium isotopes have a variety of uses, such as tracers in groundwater flow, geochronology and in radiotherapy [CHI99]. Radium is a bone tissue seeking element since it accumulates in the body according to the same pathways as calcium because of their chemical similarity [JOH97]. This makes radium especially harmful if ingested, even though it accumulates mostly in the mineral bone tissue, and not in the bone marrow [LEE05b]. Ionizing radiation is nowadays widely used for diagnostics and treatment of cancer [BRU08]. Radium has historically been the most important element in the development of radiochemistry and medical uses of ionizing radiation. In the beginning of the 20th century <sup>226</sup>Ra was used for brachytherapy, a procedure where the radiation source is placed close to the tumor. Since radium accumulates in bone tissue, it is used for the treatment of bone metastases. In radiotherapy in general, alphaemitting isotopes are preferable for the treatment of bone metastases, since radiation with sufficient range can damage the bone marrow [BRU08]. Amongst the radium isotopes, only <sup>223</sup>Ra and <sup>224</sup>Ra are suitable radionuclides for internal radiotherapy because of their appropriate short half-lives. They are both emitters of alpha particles which has a very short range ( $<100\mu$ m) in the bone tissue, since alpha-particles deposits a massive amount of energy per unit track length [BRU06]. This minimizes the damage to surrounding tissue, which is why radium-223 has recently spiked in interest as a radiopharmaceutical. In 2013 <sup>223</sup>RaCl<sub>2</sub> was approved by US Food and Drug administration as a bone seeking radiopharmaceutical for treatment of prostate cancer with skeletal metastases [PAR13].

In the 1950s it was realized that radium is a substantial environmental pollutant in tailings originating from the uranium mining industry. Radium can be also found in waste streams from other industries, e.g. in the processes of phosphate and gold mining and milling, as well as in fossil fuel combustion [DIC90]. As a consequence of these processes, radium has polluted surrounding waters and soils. Therefore, understanding of the mechanism of radium accumulation in these waste streams as well as its migration mechanisms is important for predicting and preventing excessive human exposure [DIC90].

Radium-226 decays to the noble gas radon, which can be inhaled and accumulated in lungs where it decays to polonium and subsequently a stable isotope of lead, resulting in exposure to ionizing radiation. Radon is the one of the main sources of public exposure to ionizing radiation in most countries, and a significant underlying source of lung cancer in the general population [PER94]. It is the cause for 6000-36000 deaths from lung cancer every year in the US [LUB95]. The decay-chain of <sup>226</sup>Ra ends with the stable isotope <sup>206</sup>Pb, which is the ninth daughter. As the most long-lived radioactive daughter is <sup>210</sup>Pb (t<sub>1/2</sub>=22 y), which is the sixth daughter, the first five daughters reach secular equilibrium quickly (since  $\lambda_{mother} \gg \lambda_{daughter}$ ). Ingrowth kinetics of <sup>226</sup>Ra and its daughters is shown in figure 1.



Figure 1 – Ingrowth of activity of Radium-226 daughters.

In several countries, including Sweden (SFL3-5), there are plans to build final nuclear waste repositories [SKB99]. At the Hanford Complex, the largest storage site for radioactive waste in the US, the chemical extractants used for mainly plutonium have been shown to exert a considerable influence on the containment chemistry and therefore also on the safety issues related to radioactivity release from these containments [SAM98]. Organic complexing agents also have a large influence on the migration of radionuclides [COL14][CAR98][KEI08]. For example, when migration of radionuclides from Oak Ridge National Laboratory storages has been studied, the migration of americium and curium was considerably increased due to organic ligand complexation [CAR98]. The main contributors to the organic material contents in these containments are butyl alcohol, hexone, ethylenediamineteraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid (HEDTA), tributyl phosphate and dibutyl phosphate [SAM98]. The mechanisms of migration from radioactive waste disposals are important to understand. The impact of complexing agents can be of interest under a wide range of conditions which might be relevant during the lifetime of a waste repository. Complexing reactions must therefore be understood at a fundamental level in order to model radionuclide migration in the environment [KEI08].

## 2. Background

#### 2.1 Decontamination using ethylenediaminetetraacetic acid

EDTA is amongst other organic ligands, e.g. NTA and picolinic acid, commonly used for decontamination because of its strong chelating properties [KEI08], and is therefore commonly present in nuclear waste repositories. It is estimated that in the US Department of Energy's storage tanks for radioactive waste there is 83 tons of EDTA present [SAM98], which makes thermodynamic data of EDTA important for the understanding of the overall containment chemistry. It is estimated that radium will be the main contributor to the long term radiation dose in case of containment failure of a nuclear repository [HED06][BR016]. It is therefore necessary to know radium thermodynamic properties, for example stability constants for its complex formation with EDTA, to be able to accurately model its behavior, for example its migration from wastes.

#### 2.2 Co-precipitation and dissolution of Ba(Ra)SO4

In the uranium mining industry, uranium is generally leached from the milled uranium ore or leached using sulfuric acid in situ. After the uranium leaching process, the liquid and solid residues in the tailings are neutralized and disposed of in surface ponds in a liquid waste mixture [NIR88]. The key mechanism of radium pre concentration in this process is its rapid dissolution and co-precipitation in the form of Ba(Ra)SO<sub>4</sub> [PAI98]. In these tailings, the <sup>226</sup>Ra concentration is greater than in the used uranium ore, and can reach activities of 43.4 kBq·kg<sup>-1</sup> [CAR07b]. The background radiation levels are increased by quite a large amount not only by radium, but also by its decay products, which can amount to a change from 0.1-0.2 µSv·h<sup>-1</sup> in reference areas (such as in the tailings storage region), up to 10-20 µSv·h<sup>-1</sup> on top of waste dumps [CAR07b]. In water produced in petroleum industrial processes, <sup>226</sup>Ra concentrations can reach levels up to 200 Bq·1<sup>-1</sup>, which is significantly higher than the industrial effluents limits [ZHA14]. In order to remove <sup>226</sup>Ra, sulfates are usually added to co-precipitate radium in the form of Ba(Ra)SO<sub>4</sub>. This coprecipitation of radium with barite acts mainly via an inclusion mechanism (lattice replacement) [ZHA14], and is the main mechanism which controls radium behaviour in waste streams and its environmental migration [LAN85][PAI98]. In order to be able to effectively decontaminate the uranium tailings or solid residues originating from e.g. petroleum industries, dissolution of Ba(Ra)SO<sub>4</sub> after co-precipitation is necessary. Both pure radium and barium sulfates as well as their co-precipitates are practically insoluble in aqueous solutions of mineral acids or in alkali media at room temperature [MAT16]. With the use of chelating agents, Ba(Ra)SO<sub>4</sub> can be dissolved at room temperature. The most widely used chelating agent for the dissolution of Ba(Ra)SO<sub>4</sub> is ethylenediaminetetraacetic acid (EDTA). EDTA in alkaline aqueous solutions have previously been proven to be an effective agent for dissolution of Ba(Ra)SO<sub>4</sub> [KOZ15]. At Elliot Lake, Ontario, Canada, an aqueous alkaline solution containing 0.04 M EDTA was used in the extraction of <sup>226</sup>Ra from uranium tailings, successfully extracting 80-85% of the radium [NIX83]. In the process of preparing <sup>227</sup>Ac/<sup>223</sup>Ra radiopharmaceutical generators, alkaline EDTA solutions have been used in dissolving irradiated <sup>226</sup>RaSO<sub>4</sub> targets [KUZ13]. The main reason for the high Ba(Ra)SO<sub>4</sub> solubility in alkaline EDTA solutions is the strong complex formation of  $Ba^{2+}$  and  $Ra^{2+}$  with EDTA.

#### 2.3 Stability constant determination of alkaline earth metals

Stability constants of metals with various ligands is one of the fundamental thermodynamic properties which can be used to model metal speciation in solution. Due to the high toxicity of <sup>226</sup>Ra and its daughters, access to experimental data of radium thermodynamic properties is limited. Therefore, extrapolations of ion interaction parameters from other alkaline-earth metals are often used in order to model radium [ROS11]. Since radium and barium are both alkaline-earth metals, studying them in conjunction makes it possible to investigate the effect of radii on the chemical properties of alkaline earth metals. Radium and barium have very similar chemical properties. For instance, the effective ionic radii of radium and barium in 8-fold coordination are 1.42 and 1.48 Å respectively [SHA76]. The activity coefficient ratio  $\gamma_{Ra2+}/\gamma_{Ba2+}$  is therefore often treated as unity [ROS11]. The ion interaction coefficients are necessary to describe the ionic strength dependence of the stability constants. Comparison between these SIT ion interaction coefficients has never been performed and would contribute to the solution chemistry of these elements.

Stability constants are usually determined under experimental conditions with constant ionic strength [GRE00]. In order to maintain constant ionic strength during the experimental procedure, an inert electrolyte with concentration much higher than the concentrations of the species involved in the complexation is used. These stability constants are called apparent stability constants since they are only valid under the specific experimental conditions used, since they depend on the concentration and composition of the background electrolyte. In many cases, values of thermodynamic properties, e.g, activity coefficients, cannot be directly determined experimentally, rather only changes can be measured. The changes are related to a well-defined standard state, so that the deviations can be compared.

The focus of this work is to study the complex formation between  $Ra^{2+}$ , as well as  $Ba^{2+}$ , with EDTA at different pH as a function of ionic strengths (NaCl ionic media) using an ion exchange batch technique method. The specific ion interaction theory (SIT) model is used to extrapolate the apparent stability constants of the studied complexes to a theoretical value at infinite dilution, as well as for calculating the ion interaction coefficients of the species involved in the complex formation.

### 3. Theory

#### 3.1 Activity coefficient models

Activity coefficients are used to describe deviations from ideal behavior of chemical species in solutions. The chemical activity is defined as:

$$a_i \equiv c_i \gamma_i \tag{1}$$

where  $\gamma_i$  is the activity coefficient and  $c_i$  is the concentration of species *i*. When the activity coefficient is equal to unity, the system behaves ideally and the activities of the species present in solution are equal to their respective concentrations. At very low concentrations, the activity coefficient of species in solution can be approximated as 1, since the species can be considered to behave ideally under this circumstance.

The Debye-Hückel model is the foundation for all activity coefficient models which stems from the following assumptions [LUT06][GRE00][TYA06]:

- i. All strong electrolytes are dissociated to full extent.
- ii. The interactions between ions obey Coulomb's law.
- iii. The ions can be considered point charges, where each ion is surrounded by oppositely charged ions forming an ionic atmosphere which solvent molecules are attached to.
- iv. The solvent is a continuous medium with dielectric constant  $\varepsilon$ .

These assumptions leads to the strong theoretical basis of the Debye-Hückel limiting law:

$$\log_{10}\gamma_j = -Az_j^2 \sqrt{I_m} \tag{2}$$

Where A=0.509±0.001 kg<sup>1/2</sup>·mol<sup>-1/2</sup> at 25 °C [NEA05],  $z_j$  is the electrical charge number and  $I_m$  is the ionic strength in molal units (mol·kg<sup>-1</sup>) defined as:

$$I_m = \frac{1}{2} \sum_j z_j^2 b_j \tag{3}$$

where b<sub>i</sub> is the molality (mol·kg<sup>-1</sup>) of species j. Eq. (2) is only valid for very low ionic strengths, below  $I_M=5\cdot10^{-3}$  (mol·dm<sup>-3</sup>) [STU70]. Empirical modifications can be made which extends the validity of Eq. (2) to  $I_M=0.1$  (mol·dm<sup>-3</sup>) [STU70], leading to the extended Debye-Hückel equation:

$$log_{10}\gamma_j = -\frac{Az_i^2\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \tag{4}$$

Including an ion-size parameter  $a_i$  and the constant B with a value of  $0.3283\pm0.0003 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{Å}^{-1}$  at 25 °C [NEA05]. The specific ion interaction theory (SIT) method has a much wider applicable ionic strength range for calculating activity coefficients, up to  $I_m$ =3.5 (mol·kg<sup>-1</sup>) [LUT06]. Using the SIT methodology the activity coefficient  $\gamma_j$  of an ion j with charge  $z_j$  in a solution with ionic strength  $I_m$  is expressed as:

$$log_{10}\gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I_m)m_k$$
<sup>(5)</sup>

where  $\varepsilon(j,k,I_m)$  is the empirical ion interaction coefficient,  $m_k$  is the molality of ion k and D is the Debye-Hückel term which is defined as:

$$D = \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \tag{6}$$

where the value of 1.5 is an empirical parameter chosen to minimize the effect of ionic strength on the ion interaction coefficients [GRE00]. The ion interaction coefficients have a slight dependence on ionic strength which can be considered negligible for ionic strengths below 3.5 mol·kg<sup>-1</sup> when using 1:1, 1:2 and 2:1 electrolytes, but ionic strength corrections can be made by expressing the ion interaction coefficients in two terms, one independent and one dependent on the ionic strength [GRE00].

#### 3.2 Stability constants of a complex formation reaction

A general complex formation reaction can be expressed as:

$$mM + qL + nH_20 \rightleftharpoons M_m L_q(0H)_n + nH \tag{7}$$

where M is a metal ion, L is a ligand and  $M_mL_q(OH)_n$  is the formed complex [GRE00], charges have been omitted for brevity. The apparent stability constant  $\beta_{q,n,m}$  of the complex formation is defined in terms of concentrations between the products and reactants in Eq. (7) according to:

$${}^{*}\beta_{q,n,m} = \frac{\left[M_{m}L_{q}(OH)_{n}\right][H^{+}]^{n}}{[M]^{m}[L]^{q}}$$
(8)

Expressing the stability constant in terms of activities instead yields the stability constant at zero ionic strength, which is defined as:

$${}^{*}\beta_{q,n,m}^{0} = \frac{\left[M_{m}L_{q}(OH)_{n}\right][H^{+}]^{n}}{[M]^{m}[L]^{q}}\frac{\gamma_{q,n,m}\gamma_{H^{+}}^{n}}{\gamma_{m}^{M}\gamma_{I}^{q}}$$
(9)

Substituting the concentrations with the apparent stability constant defined in Eq. (8) yields:

$${}^{*}\beta^{0}_{q,n,m} = {}^{*}\beta_{q,n,m} \frac{\gamma_{q,n,m} \gamma^{n}_{H^{+}}}{\gamma^{m}_{M} \gamma^{q}_{L}}$$
(10)

Taking the logarithm of both sides of Eq. (10) yields:

$$\log_{10}{}^*\beta_{q,n,m}^0 = \log_{10}{}^*\beta_{q,n,m} - m\log_{10}\gamma_M - q\log_{10}\gamma_M + \log_{10}\gamma_{q,n,m} + n\log_{10}\gamma_{H^+}$$
(11)

Eq. (11) can be rewritten by substituting the activity coefficients by the SIT model definition defined in Eq. (5) [LUT06]:

$$\log_{10}{}^{*}\beta_{q,n,m} - \Delta z^{2}D = \log_{10}{}^{*}\beta_{q,n,m}^{0} - \Delta \varepsilon I_{m}$$
(12)

where

$$\Delta z^{2} = (z_{complex})^{2} + n - mz_{m}^{2} - qz_{L}^{2}$$
(13)

$$\Delta \varepsilon = \varepsilon(complex, N \text{ or } X) - q\varepsilon(N, L) - m\varepsilon(M, X) + n\varepsilon(H, X)$$
(14)

#### 3.3 Stability constant determination using ion exchange distribution method

A sodium ion form cation exchange resin exchanges its sodium ion with a cation  $M^{m+}$  in aqueous phase according to:

$$z\overline{[Na^+]} + [M^{z+}] \rightleftharpoons \overline{[M^{z+}]} + z[Na^+]$$
(15)

Where the bar superscript indicates resin phase. The distribution ratio, D, between a resin phase and an aqueous phase is defined as:

$$D = \frac{Specific radioactivity in resin phase}{Specific radioactivity in aqueous phase}$$
(16)

Where the specific radioactivity is the radioactivity per unit volume or unit mass. Measurements of the radioactivity in the aqueous phase allows for calculation the distribution ratio, D, between the resin phase and the aqueous phase, according to:

$$D = \left(\frac{A_0 - A_f}{A_f}\right) \left(\frac{V}{w}\right) \tag{17}$$

where the unit of D is in mL/g,  $A_0$  is the total radioactivity of the radioisotope in the sample volume,  $A_f$  is the radioactivity of the radioisotope in the aqueous phase after equilibrium has been reached, V is the solution volume and *w* is the weight of the dry resin [GAL78]. The complex formation reaction in Eq. (7) where M is an alkaline earth metal ion and L=H<sub>r</sub>EDTA<sup>(r-4)</sup> is expressed as:

$$mM^{2+} + qH_rEDTA^{(r-4)} \approx \left[M_m (H_{(r-n)}EDTA)_q\right]^{(2m+q(r-n-4))} + nH^+$$
 (18)

with a stability constant  $\beta_{q,r,m}$ , where it is assumed that no hydrolysis occurs. The distribution coefficient of  $M^{2+}$  between the resin and the aqueous phase in the absence of ligand can be expressed by [GAL78]:

$$\lambda = \frac{\overline{[M^{2+}]}}{[M^{2+}]} \frac{V}{w} \tag{19}$$

For the investigated system this can be expressed as:

$$D = \frac{\overline{[M^{2+}]}}{\sum_{q,r=0,m=1}^{\infty} \left( m \left[ M_m (H_{(r-n)} E DTA)_q \right]^{(2m+q(r-n-4))} \right)^W}$$
(20)

In this expression when q=0, the concentration term becomes equal to  $[M^{2+}]$ , since there is no ligand involved, and there are no free metal ions with m>1. Under these circumstances, i.e. if q=0, Eq (20) becomes equal to the definition of  $\lambda$  shown in Eq. (19). Eq. (19) also allows for expressing the resin M<sup>2+</sup> concentration as:

$$\overline{[M^{2+}]} = \lambda [M^{2+}] \frac{w}{V}$$
<sup>(21)</sup>

The stability constant  $\beta_{q,r,m}$  can be defined through the reaction of formation for the complex  $\left[M_m(H_{(r-n)}EDTA)_a\right]^{(2m+q(r-n-4))}$  according to:

$$\beta_{q,r,m} = \frac{\left[M_m \left(H_{(r-n)} E D T A\right)_q\right]^{(2m+q(r-n-4))}}{\left[M^{2+}\right]^m \left[H_{(r-n)} E D T A^{(r-n-4)}\right]^q}$$
(22)

This allows for expressing the concentration of  $\left[M_m (H_{(r-n)} EDTA)_q\right]^{(2m+q(r-n-4))}$  as:

$$\left[M_m(H_r E D T A)_q\right]^{(2+q(r-4))} = \beta_{q,r,m} [M^{2+}]^m \left[H_r E D T A^{(r-4)}\right]^q$$
(23)

Substituting the resin  $M^{2+}$  concentration with the expression in Eq. (21) and the concentration from Eq. (23) into Eq. (20) yields:

$$D = \frac{\lambda[M^{2+}]}{[M^{2+}] + \sum_{q,r=0,m=1} \left(\beta_{q,r,m}[M^{2+}]^m [H_r E DT A^{(r-4)}]^q\right)}$$
(24)

Assuming that only mononuclear complexes, m=1 are formed under the studied experimental conditions [GAL78], the  $M^{2+}$  concentration can be cancelled from Eq. (24) resulting in:

$$D = \frac{\lambda}{1 + \sum_{q,r} \beta_{q,r,1} [H_r E DT A^{(r-4)}]^q}$$
(25)

Rewriting this expression as the stability constant as a function of the distribution yields:

$$D\left(1 + \sum_{q,r} \beta_{q,r,1} \left[H_r E D T A^{(r-4)}\right]^q\right) = \lambda$$

$$\sum_{q,r} \beta_{q,r,1} \left[H_r E D T A^{(r-4)}\right]^q = \frac{\lambda}{D} - 1$$
(27)

By measuring the distribution ratio under varying ligand concentrations,  $[H_rEDTA^{(r-4)}]$  can be related to the apparent stability constants  ${}^*\beta_{1,r,1}$  according to Eq. (28):

$$\sum_{r} \left(\beta_{1,r,1} \left[H_r E D T A^{(r-4)}\right]\right) + 1 = \frac{\lambda}{D}$$
<sup>(28)</sup>

where it has been assumed that only one ligand molecule is included in each complex.

#### 3.4 Ethylenediaminetetraacetic acid (EDTA)

Ethylenediaminetetraacetic acid, (CH<sub>2</sub>COOH)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>COOH)<sub>2</sub>, henceforth referred to as EDTA, is a polyaminocarboxylate that forms strong complexes with a variety of cations [GHA09]. It is a hexadentate ligand, i.e. it has six donor groups with which it binds to a central cation to form a complex. EDTA is resilient to radiation-induced degradation as well as to high temperatures as it will not degrade until temperatures of 200-250° C [KEI08]. It can act as a double zwitterion, i.e. it is able to hold both positive and negative charges by redistributing electrons, contributing to its chemical stability and resilience to biodegradation [NEA05][ZAI97]. Pure H<sub>4</sub>EDTA has very low solubility in water, therefore, Na<sub>2</sub>EDTA·2H<sub>2</sub>O is commonly used for preparation of aqueous EDTA solutions. Na<sub>2</sub>EDTA·2H<sub>2</sub>O has a density of 1.01 g/cm<sup>3</sup> and molar mass of 372.24 g/mole [NEA05].

EDTA has six protonation constants:

$$H_r EDTA^{(r-4)} + H^+ \rightleftharpoons H_{(r+1)} EDTA^{(r-3)}$$
<sup>(29)</sup>

The protonation constants,  $K_r^{\circ}$  of the reaction in Eq. (29) at zero ionic strength and 25°C are listed in table 1.

r	$\log_{10}$ K $_r^0$	$\log_{10}\beta_r^0$
1	(11.24±0.03)	(11.24±0.03)
2	(6.80±0.02)	(18.04±0.04)
3	(3.15±0.02)	(21.19±0.04)
4	(2.23±0.05)	(23.42±0.07)
5	(1.3±0.1)	(24.72±0.12)
6	-(0.5±0.2)	(24.22±0.23)

Table 1 – Stability constants for the protonation of  $H_{(r-1)}EDTA^{(r-5)}$  at zero ionic strength [NEA05].

The protonation constants K<sub>r</sub> can be expressed as acid dissociation constants, K<sub>a</sub>, through:

$$K_a = \frac{1}{K_r} \tag{30}$$

Applying the SIT methodology, the protonation constants at zero ionic strength are extrapolated to the ionic strengths used in this work. Extrapolating using the SIT methodology defined by Eq. (12) yields:

$$log_{10}K_{a,r} = log_{10}K_{a,r}^0 - \Delta\varepsilon I_m + \Delta z^2 D$$
(31)

The ion interaction coefficient term as defined in SIT (Eq. (14)) for reaction (29) can thus be calculated as:

$$\Delta \varepsilon = \varepsilon \left( H_{(r+1)} E DT A^{(r-3)}, Na^+ \right) - \varepsilon \left( H_r E DT A^{(r-4)}, Na^+ \right) - \varepsilon \left( H^+, Cl^- \right)$$
(32)

Interaction	Specific ion interaction coefficient
ε(EDTA <sup>4-</sup> ,Na <sup>+</sup> )	(0.32±0.14)
ε(HEDTA <sup>3-</sup> ,Na <sup>+</sup> )	-(0.1±0.14)
$\epsilon$ (H <sub>2</sub> EDTA <sup>2-</sup> ,Na <sup>+</sup> )	-(0.37±0.14)
ε(H <sub>3</sub> EDTA <sup>-</sup> ,Na <sup>+</sup> )	-(0.33±0.14)
ε(H <sub>4</sub> EDTA,NaCl)	-(0.29±0.14)
$\epsilon(H_5EDTA^+,Cl^-)$	-(0.23±0.15)
$\epsilon(H_6EDTA^{2+},Cl^{-})$	-(0.20±0.16)
ε(H <sup>+</sup> ,Cl <sup>−</sup> )	(0.12±0.01)

where the ion interaction coefficients for r=0,1,...,5 used in Eq. (29) are presented in table 2 [NEA05]: Table 2 – Ion interaction coefficients for  $H_{(r-1)}EDTA^{(r-5)}$  protonation constants in conjunction with the ionic media NaCl.

The ionic strength dependence of the pKa values of the protonation reaction shown in Eq. (29) for r=0,1,..,5 can be seen in table 3.

Table 3 - pKa values extrapolated to different ionic strengths for the different values of r in Eq. (29).

$I_m$	pKa,	pKa,	pKa,	pKa,	pKa,	pKa,
$(mol \cdot kg^{.1})$	r=0	r=1	r=2	r=3	r=4	r=5
0.00	11.24	6.80	3.15	2.23	1.30	-0.50
0.22	10.24	6.05	2.61	1.13	0.20	-1.60
0.51	10.11	5.95	2.49	0.87	-0.07	-1.86
1.02	10.16	5.97	2.41	0.68	-0.27	-2.04
2.09	10.51	6.22	2.39	0.54	-0.43	-2.17
2.64	10.74	6.39	2.40	0.52	-0.47	-2.19

The acid dissociation constants of EDTA are utilized for the construction of speciation curves at the different ionic strengths.

$$K_{a,r} = \frac{\left[H_r E D T A^{(r-4)}\right] [H^+]}{\left[H_{(r+1)} E D T A^{(r-3)}\right]}$$
(33)

The molar fraction  $x_{HrEDTA(r-4)}$  is expressed in Eq. (34):

$$x_{H_r EDTA^{(r-4)}} = \frac{\left[H_r EDTA^{(r-4)}\right]}{\sum_{i=0}^{i=6}[H_i EDTA^{(i-4)}]}$$
(34)

Expressing the terms H<sub>r</sub>EDTA<sup>(r-4)</sup> in terms of EDTA<sup>4-</sup> through:

$$\left[H_r E D T A^{(r-4)}\right] = \frac{\left[E D T A^{4-}\right] \left[H^+\right]^r}{\prod_{i=1}^{i=r} K_{a,j}}$$
(35)

Eq. (34) can then be expressed as:

$$x_{H_{r}EDTA^{(r-4)}} = \frac{[H^{+}]^{r} / \prod_{i=1}^{i=r} K_{a,i}}{\sum_{j=1}^{j=7} \frac{[H^{+}]^{(j-1)}}{\prod_{i=1}^{i=j-1} K_{a,i}}}$$
(36)

Solving Eq. (36) for the different molar fractions using the SIT interaction coefficients established by OECD NEA [NEA05], together with the acid dissociation constants of EDTA presented in table 3, a speciation curve with molar fraction against  $-\log_{10}[H^+]$  can be constructed at any ionic strength (below  $I_m$ =3.50 (mol·kg<sup>-1</sup>) [GRE00]) using the SIT methodology. The speciation curve at I<sub>m</sub>=0.22 (mol·kg<sup>-1</sup>) is shown in figure 2 as an example.



Figure 2 – Speciation curve at  $I_m$ =0.22 mol·kg<sup>-1</sup>, where the molar fractions of the different EDTA species are shown as a function of the hydrogen ion concentration.

In order to study the complex formation of the metal ion with the EDTA<sup>4-</sup> form only, it is necessary to maintain  $-\log_{10}[H^+]=12.4$  or higher, at  $I_m=0.22$  (mol·kg<sup>-1</sup>), because as shown in figure 2 the EDTA<sup>4-</sup> form is dominant at  $-\log_{10}[H^+]$  values higher than 12. The HEDTA<sup>3-</sup> form is dominant around  $-\log_{10}[H^+]=8$  at ionic strength  $I_m=0.22$  (mol·kg<sup>-1</sup>). As the K<sub>a,i</sub> values are ionic strength dependent, the  $-\log_{10}[H^+]$  value at which the HEDTA<sup>3-</sup> form is maximized depends on the ionic strength. In order to practically determine the molar fractions using Eq. (36), a pH electrode has to be calibrated in hydrogen concentration scale to avoid the ionic strength dependence of the hydrogen ions (as pH is defined as the chemical activity of the hydrogen ions). The substitution of the electrolyte with ligand can effectively be neglected as long as the ligand concentration does not exceed 10% of the total concentration [SPA98].

#### 3.5 Corrections for ligand ionic media complex formation

The apparent stability constants needs to be corrected for the NaEDTA<sup>3-</sup> complex formation, since the amount of free ligand  $H_rEDTA^{(r-4)}$  that can form complex with the metal ion  $M^{2+}$  is decreased by the following reaction:

$$Na + H_r EDTA^{(r-4)} \rightleftharpoons [NaH_r EDTA]^{(r-3)}$$
(37)

As the concentration of Na<sup>+</sup> is considerably higher than the M<sup>2+</sup> concentration under all experimental conditions, this effect has to be accounted for even though the stability constant of this reaction is low, with a value of  $log_{10}K^{0}_{NaEDTA}$ =(2.8±0.2) at zero ionic strength [NEA05]. The total EDTA concentration in the studied system can in the  $-log_{10}[H^{+}]$  range 8.0-12.4 be expressed as:

$$\begin{bmatrix} H_r EDTA^{(r-4)} \end{bmatrix}_{tot} = \begin{bmatrix} EDTA^{4-} \end{bmatrix} + \begin{bmatrix} HEDTA^{3-} \end{bmatrix} + \begin{bmatrix} H_2 EDTA^{2-} \end{bmatrix} + \begin{bmatrix} MEDTA \end{bmatrix}^{2-}$$
(38)  
+ 
$$\begin{bmatrix} MHEDTA \end{bmatrix}^{-} + \begin{bmatrix} NaEDTA \end{bmatrix}^{3-} + \begin{bmatrix} NaHEDTA \end{bmatrix}^{2-}$$

since the other forms of  $H_rEDTA^{(r-4)}$  are negligible in the specified pH interval. The metal ion concentrations are only in trace amounts which makes the  $MH_rEDTA^{(r-2)}$  concentration negligible compared to the other concentrations. HEDTA<sup>3-</sup> and H<sub>2</sub>EDTA<sup>2-</sup> concentrations can be expressed in terms of EDTA<sup>4-</sup> concentration according to Eq. (39).

$$K_{a,r} = \frac{\left[H_r E D T A^{(r-4)}\right] [H^+]}{\left[H_{(r+1)} E D T A^{(r-3)}\right]}$$
(39)

Similarly, the MEDTA<sup>2-</sup>, concentration is expressed in terms of EDTA<sup>4-</sup> concentration:

$$[MEDTA]^{2-} = \beta_{MEDTA}[M^{2+}][EDTA^{4-}]$$
(40)

From Eq. (37) the NaEDTA<sup>3-</sup> and NaHEDTA<sup>2-</sup> concentrations can also be expressed in this manner. Substituting the terms in the total  $H_rEDTA^{(r-4)}$  concentration expression yields:

$$\begin{bmatrix} H_r EDTA^{(r-4)} \end{bmatrix}_{tot} = \begin{bmatrix} EDTA^{4-} \end{bmatrix} + \frac{\begin{bmatrix} EDTA^{4-} \end{bmatrix} \begin{bmatrix} H^+ \end{bmatrix}}{K_{a,1}} + \frac{\begin{bmatrix} EDTA^{4-} \end{bmatrix} \begin{bmatrix} H^+ \end{bmatrix}^2}{K_{a,1} \cdot K_{a,2}} + \beta_{MEDTA} \begin{bmatrix} M^{2+} \end{bmatrix} \begin{bmatrix} EDTA^{4-} \end{bmatrix} + K_{NaEDTA} \begin{bmatrix} Na^+ \end{bmatrix} \begin{bmatrix} EDTA^{4-} \end{bmatrix} \begin{bmatrix} H^+ \end{bmatrix}$$

$$+ \beta_{MEDTA} \begin{bmatrix} M^{2+} \end{bmatrix} \begin{bmatrix} EDTA^{4-} \end{bmatrix} + K_{NaEDTA} \begin{bmatrix} Na^+ \end{bmatrix} \begin{bmatrix} EDTA^{4-} \end{bmatrix} + K_{NaHEDTA} \frac{\begin{bmatrix} Na^+ \end{bmatrix} \begin{bmatrix} EDTA^{4-} \end{bmatrix} \begin{bmatrix} H^+ \end{bmatrix}}{K_{a,1}}$$

$$(41)$$

The metal ion concentrations are only in trace amounts which makes the MEDTA<sup>2-</sup> concentration negligible compared to the other terms. The EDTA<sup>4-</sup> concentration can therefore be expressed as:

$$[EDTA^{4-}] = \frac{\left[H_r EDTA^{(r-4)}\right]_{tot}}{1 + \frac{[H^+]^2}{K_{a,1}} + \frac{[H^+]^2}{K_{a,2}} + K_{NaEDTA}[Na^+] + K_{NaHEDTA}\frac{[Na^+][H^+]}{K_{a,1}}}$$
(42)

At  $-\log_{10}[H^+] \ge 12$  the H<sub>r</sub>EDTA<sup>(r-4)</sup> concentrations for r $\neq 0$  can be considered negligible, and the total EDTA concentration can therefore be expressed in even simpler terms:

$$\left[H_{r}EDTA^{(r-4)}\right]_{tot} = \left[EDTA^{4-}\right] + \left[NaEDTA^{3-}\right]$$
(43)

The EDTA<sup>4-</sup> concentration can similarly be expressed as:

$$[EDTA^{4-}] = \frac{\left[H_r EDTA^{(r-4)}\right]_{tot}}{\left(1 + \beta_{NaEDTA}[Na^+]\right)}$$
(44)

The apparent stability constants  $\beta_{MEDTA}$  can then be corrected for the NaEDTA complexation according to:

$$\beta_{MEDTA} = \frac{[MEDTA]^{2^{-}}}{[M^{2^{+}}][EDTA^{4^{-}}]} = \frac{[MEDTA]^{2^{-}}}{[M^{2^{+}}]\frac{[H_{r}EDTA^{(r-4)}]_{tot}}{(1+\beta_{NaEDTA}[Na^{+}])}} = \frac{[MEDTA]^{2^{-}}(1+\beta_{NaEDTA}^{app}[Na^{+}])}{[H_{r}EDTA^{(r-4)}]_{tot}[M^{2^{+}}]}$$
(45)

Expressing the term

$$\frac{[MEDTA]^{2-}}{[H_r EDTA^{(r-4)}]_{tot}[M^{2+}]} = \beta_{MEDTA}^{tot}$$
(46)

Allows for expressing the apparent stability constant in terms of the total H<sub>r</sub>EDTA<sup>(r-4)</sup> concentration:

$$\beta_{MEDTA} = \beta_{MEDTA}^{tot} \left( 1 + \beta_{NaEDTA}^{app} [Na^+] \right)$$
(47)

$$log_{10}\beta_{MEDTA} = log_{10}\beta_{MEDTA}^{tot} + log_{10}(1 + \beta_{NaEDTA}[Na^+])$$

$$\tag{48}$$

which is similar to the suggested (and fairly simplified) NaEDTA<sup>3-</sup> correction procedure presented by OECD NEA in their extensive EDTA-review [NEA05].

#### 3.6 pH titration

Nernst equation describes the potential change as a function of the reaction quotient of species *j* [ATK09]:

$$E = E_0 + \frac{RT}{nF} \cdot \ln Q_j \tag{49}$$

For a pH-electrode, this can be expressed in terms of the hydrogen activity according to Eq (50):

$$E = E_0 + \frac{RT}{nF} \cdot \ln\{H^+\}$$
(50)

The natural logarithm can be expressed as the logarithm in base 10 as:

$$ln\{H^+\} = log_{10}\{H^+\} \cdot ln(10) \tag{51}$$

Substituting this expression into Eq. (50) results in:

$$E = E_0 + \ln(10) \cdot \frac{RT}{nF} \cdot \log\{H^+\}$$
(52)

The activity of hydrogen can be expressed as the hydrogen concentration and activity coefficient:

$$E = E_0 + \ln(10) \cdot \frac{RT}{nF} \cdot \log[H^+] + \ln(10) \cdot \frac{RT}{nF} \cdot \log\gamma_{H^+}$$
(53)

The titrations are performed at five different ionic strengths, where the ionic strength and temperature is maintained constant throughout the titration. The term containing the activity coefficient in Eq. (53) is therefore maintained constant throughout every individual titration and the invariable terms can be summed together:

$$E_0^* = E_0 + \ln(10) \cdot \frac{RT}{nF} \cdot \log \gamma_{H^+}$$
(54)

which results in Eq (55):

$$E = E_0^* + \ln(10) \cdot \frac{RT}{nF} \cdot \log[H^+]$$
(55)

The potential *E* is linearly dependent on the hydrogen concentration, making it possible to calibrate the pH electrode in the concentration scale if the ionic strength is constant as the titration volume is changed. Since the  $E_0$  value is a characteristic of the pH electrode, the change in  $E_0^*$  can be attributed to the change in activity coefficient because of the ionic strength difference between titrations. Using the SIT equation, Eq. (5), for the activity coefficient calculations, the activity coefficient change can be attributed to the change in the Debye-Hückel term as well as in the ion interaction coefficient term. The Debye-Hückel term is known for all ionic strengths, which makes it possible to calculate the ion interaction coefficient is calculated by minimizing the error squares sum from Eq. (56):

$$S = \sum (\gamma_{experimental,i} - \gamma_{calculated,i})^2$$
(56)

## 4. Experimental

#### 4.1 Materials and Methods

The complex formations were studied in duplicate series, where each series contained 11 samples per ionic strength, at the ionic strengths: 0.22, 0.5, 1.0, 2.0 and 2.5 mol·dm<sup>-3</sup>. Cation exchange resin (Biorad AG 50W-X8 Resin 200-400 Mesh in sodium form) was added to each sample in order to distribute the alkaline earth metal ions between the aqueous phase and the resin phase. Eckert & Ziegler Isotope Products <sup>133</sup>BaCl<sub>2</sub> ( $t_{1/2}$ =10.54 y [KAR15]) stock solution was used, which also contained barium carrier, resulting in an activity of 3.7·10<sup>4</sup> Bq per sample. Radium stock solutions were prepared from dissolved RaCO<sub>3</sub> powder according to the previously established procedure [MAT16], resulting in a specific activity of <sup>226</sup>Ra of 2.51·10<sup>4</sup> Bq·µl<sup>-1</sup>. Due to the high radioactivity of <sup>133</sup>Ba and <sup>226</sup>Ra stock solutions, radiation protection measures had to be taken during the experimental work to minimize potential risks. All measurements and calculations throughout this study have been done at 25.1 °C unless specified otherwise.

All aqueous solutions were prepared using MQ water with resistivity equal to 18.2 M $\Omega$ ·cm at 25°C and total organic content < 5mg/l. Ionic strength was adjusted using NaCl stock solution prepared using solid NaCl (Sigma-Aldrich ACS reagent p.a. ≥99.0 %). Ethylenediaminetetraacetic acid (EDTA), stock solutions were prepared from solid Na<sub>2</sub>EDTA·2H<sub>2</sub>O (Sigma p.a.  $\geq$ 99.0 %). In order to study the complexation of the EDTA<sup>4-</sup> form, the pH was increased by adding 50 µl of 5M NaOH stock solution prepared from Sigma-Aldrich fixanal to each sample of the  $Ba^{2+}$  series and 5 µl to each sample of the  $Ra^{2+}$  series. When studying the HEDTA<sup>3-</sup> complexation, the pH was adjusted in order to maximize the HEDTA<sup>3-</sup> form, according to Eq. (36). The  $H_r EDTA^{(r-4)}$  total concentrations were varied throughout the sample series ranging between 0 and 6.67·10<sup>-5</sup> mol·dm<sup>-3</sup>. Samples without ion exchange resin and ligand concentration were prepared in order to measure the total sample radioactivity. The total aqueous volumes were adjusted to 10 and 1 ml, for the Ba<sup>2+</sup> and Ra<sup>2+</sup> series respectively, using NaCl stock solution and MQ water. The pH electrode was calibrated using Certipur Merck pH 4, 7 and 10 buffers, and a potentiometric titration was performed in order to calibrate the electrode in the concentration scale. For all [BaHrEDTA]<sup>(r-2)</sup> complex formation measurements, 50 µl of the aqueous phase was extracted from each sample and added to a 7 ml LSC-vial and subsequently mixed with Emulsifier safe LSC cocktail. For the [RaHrEDTA]<sup>(r-2)</sup> measurements, 10 µl of the aqueous phase was extracted from each sample and added to a plastic vial containing 1 ml of 4M HCl prepared from Sigma-Aldrich fixanal. As the equilibration time of the complex formation is rather slow, the samples had to be shaken several times to speed up the equilibrium (see Appendix A for more information).

The potentiometric titrations required preparation of 10 ml samples with the appropriate ionic strengths at  $-\log_{10}[H^+]\approx 2.6$ , by adding 5 µl of 5M Sigma-Aldrich fixanal HCl solution to 9.998 ml NaCl solution. The titrated solution was measured with the specified pH electrodes while a few µl of 0.1M NaOH solution was added and the potentiometric values were noted between additions. Plotting  $-\log_{10}[H^+]$  against voltage, the data was fitted linearly according to Eq. (. From the fitted equation the corresponding potential to the required hydrogen concentration was calculated. The measurement series were then adjusted to the calculated potential required to maximize the molar fraction of the HEDTA<sup>3-</sup> form.

#### 4.2 Apparatus

Resin and all other solid chemicals used were weighed on a Sartorius Quintix125D-1S scale. The barium samples were measured using a Perkin Elmer Guardian 1414 Liquid Scintillation Counter. The radium samples were measured using a Canberra DSA-2000/A coupled with Canberra GEM23195 closed-end coaxial HPGe detector (53.5 mm diameter, 63.1 mm length) and a digital spectrum analyzer Ortec DSPEC50 coupled to an Ortec GEM-C5060 coaxial HPGe detector (50.5 mm diameter, 68.3 mm length) with a 0.9 mm carbon epoxy entrance window. The detectors were calibrated using a NIST traceable, Eckert and Ziegler radionuclide reference solution. The spectra obtained from the measurements were analyzed using Gamma Vision 7.01.03, and Apex Gamma software. The 827 pH lab Metrohm pH meter and Metrohm Primatrode with NTC electrode was used for the potentiometric measurements.

## 5. Results

#### 5.1 Titration curves

The potentiometric titration curve at  $I_m$ =2.5 (mol·kg<sup>-1</sup>) is shown in figure 3. The equation shown in figure 3 is obtained from least squares fitting and is used to calculate the potential corresponding to the desired hydrogen concentration [GRA52]. The potentiometric titrations were performed at 23±1°C with very small changes in volume and at constant ionic strengths. The slope obtained in the potentiometric measurement is in agreement with the theoretical value at 25 °C of 59.16 [ATK09]. Linear regressions of the potentiometric titrations were performed at every ionic strength used, which all had a high coefficients of determination, r<sup>2</sup> [MIL02], and slopes close to the theoretical value, indicating accurate potentiometric titrations [SOK01].



Figure 3 – Potentiometric titration curve at  $I_m=2.5 \text{ mol}\cdot kg^{-1}$ .

$I_m (\mathrm{mol}\cdot\mathrm{kg}^{-1})$	Intercept	Slope	$r^2$
0.22	386.61±2.82	58.08±0.36	1.000
0.51	386.85±6.20	$58.72 \pm 0.85$	0.999
1.02	392.82±2.81	57.51±0.36	1.000
2.09	404.02±5.19	$58.08 \pm 0.62$	0.999
2.64	411.13±2.07	57.87±0.25	1.000

Table 4 - The potentiometric titration results for the different ionic strengths with  $2\sigma$  standard deviations of the linear fit, performed at  $23\pm 1^{\circ}$ C.

Applying Nerst equation to the potentiometric calibration data, the ion interaction coefficient,  $\epsilon$ (H<sup>+</sup>,Cl<sup>-</sup>), can be calculated using the SIT methodology in conjunction with least squares fitting, as the difference in intercept between ionic strengths is a function of the activity coefficient according to Eq. (57):

$$E_0^* = E_0 + \ln(10) \frac{RT}{nF} \log \gamma_{H^+}$$
(57)

According to the SIT theory the activity coefficient is expressed through Eq. (5), which makes it possible to make an arbitrary starting guess of  $\epsilon$ (H<sup>+</sup>,Cl<sup>-</sup>) and iterate with the least squares method applied to the experimental data and the value calculated from the starting guess according to:

$$S = \sum (\gamma_{H+,exp,i} - \gamma_{H+,calc,i})^2$$
(58)

Taking into account only the standard deviations of the fit for the intercept and the slope, the ion interaction coefficient is calculated with standard deviation as  $\epsilon(H^+,Cl^-)=(0.123\pm0.002)$ . The value is in excellent agreement with literature data, e.g. in the OECD NEA chemical thermodynamic database [NEA05]  $\epsilon(H^+,Cl^-)=(0.12\pm0.01)$ . This indicates that the potentiometric titrations performed are reliable and in agreement with literature.

#### 5.2.1 Stability constant determination

By measuring the distribution ratio under varying ligand concentrations,  $[H_rEDTA^{(r-4)}]$  can be related to the apparent stability constants  $\beta_{I,r,I}$  according to Eq. (28):

$$\sum_{r} (\beta_{1,r,1} [H_r E DT A^{(r-4)}]) + 1 = \frac{\lambda}{D}$$
(28)

At  $-\log_{10}[H^+]=12.4$ , the EDTA<sup>4-</sup> form is dominant according to Eq. (36) with a molar fraction  $\ge 98\%$  at every ionic strength studied. Ionic strengths were recalculated to molal from molar using conversion factors established by [GUI03]. The apparent stability constants can under these conditions be determined through applying a least squares fit to the distribution ratios against the EDTA<sup>4-</sup> concentration, which yields a linear regression with slope equal to  $\beta_{MEDTA}$ .

In the  $\beta_{MHEDTA}$  stability constant determination, corrections for the molar fraction of the EDTA<sup>4-</sup> form has to be made, since the HEDTA<sup>3-</sup> form cannot reach a molar fraction  $\geq$ 99% according to Eq. (36). The

influence of  $H_2EDTA^{2-}$  is considered negligible, since it expectedly forms considerably weaker complexes than the EDTA<sup>4-</sup> form.

### 5.2.2 BaEDTA<sup>2-</sup> stability constant determination

At ionic strengths  $I_m$ =0.22, 0.50, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>) the distribution ratios of <sup>133</sup>Ba are plotted against [H<sub>r</sub>EDTA<sup>(r-4)</sup>]<sub>tot</sub> and shown in figure 4.



Figure 4 – Determination of apparent stability constants for BaEDTA<sup>2-</sup> in the linear regressions by least squares fitting at  $I_m$ =0.22, 0.50 (a), 1.02, 2.09 (b), and 2.64 (mol·kg<sup>-1</sup>) (c) according to Eq. (28). The  $2\sigma$  confidence bounds of the fit are the dotted lines and the uncertainties correspond to standard deviation based on duplicate samples.

Since the apparent stability constants in Fig. 4 are determined as a function of the total  $H_rEDTA^{(r-4)}$  concentration, a correction for both the sodium complex formation with EDTA as well as EDTA-

protonation is required to find the apparent stability constants of BaEDTA<sup>2-</sup>, according to section 3.4. According to Eq. (42), the relationship between  $[H_rEDTA^{(r-4)}]_{tot}$  and  $[EDTA^{4-}]$  is expressed as:

$$[EDTA^{4-}] = \frac{\left[H_r EDTA^{(r-4)}\right]_{tot}}{1 + \frac{[H^+]^2}{K_{a,1}} + \frac{[H^+]^2}{K_{a,2}} + K_{NaEDTA}[Na^+] + K_{NaHEDTA}\frac{[Na^+][H^+]}{K_{a,1}}}$$
(42)

Stability constants for the NaEDTA<sup>3-</sup> complexation are available in literature at various ionic strengths [NEA05], which are shown in table 5 together with the Debye-Hückel term, D defined in Eq. (6).

$I_m (mol \cdot kg^{-1})$	log <sub>10</sub> KNaEDTA [NEA05]	Debye-Hückel term, D
0.00	(2.80±0.20)	0.000
0.10	(1.95±0.21)	0.110
0.25	(1.71±0.23)	0.146
0.51	(1.54±0.31)	0.175
0.76	(1.47±0.41)	0.192
1.02	(1.45±0.52)	0.204
2.09	$(1.50 \pm 1.00)$	0.232
3.20	$(1.70 \pm 1.70)$	0.247

Table 5 - K<sub>NaEDTA</sub> values taken from literature together with corresponding Debye-Hückel terms

Using the SIT methodology, the values of  $K_{NaEDTA}$  found in literature can be extrapolated to the ionic strengths used in this work that are not available in literature. The slope  $\Delta \epsilon$ =-0.27±0.33 was found to fit the data in table 5 very well providing  $K_{NaEDTA}$  at every ionic strength used in this work. If available, uncertainties were taken from literature [NEA05], and were otherwise propagated using the SIT methodology with  $\Delta \epsilon$ =-0.27±0.33.

Table 6 - K<sub>NaEDTA</sub> calculated using the SIT methodology with a slope  $\Delta \epsilon$ =-0.27±0.33

$I_m (mol \cdot kg^{-1})$	Extrapolated K <sub>NaEDTA</sub>
0.217	$(1.74\pm0.23)^{a}$
0.506	(1.54±0.31)
1.022	(1.44±0.52)
2.086	(1.50±1.00)
2.637	$(1.59 \pm 1.30)^{a}$

<sup>a</sup>Uncertainties were propagated from used literature ion interaction coefficients

Eq. (42) was then used to convert the  $[H_rEDTA^{(r-4)}]_{tot}$  term into the corresponding EDTA<sup>4-</sup> concentration. The NaEDTA<sup>3-</sup> complex formation, is a substantial contribution to the denominator on the right hand side of Eq. (42), meaning it consumes a large fraction of the free EDTA<sup>4-</sup> concentration. The uncertainties for the apparent K<sub>NaEDTA</sub>-values as seen in table 5 are large, and will account for a large part of the uncertainty of the corrected apparent stability constants. The stability constant at zero ionic strength,  $\beta^{\circ}_{BaEDTA}$  is calculated using the SIT methodology applied to the determined apparent stability constants according to Eq. (12):

$$\log_{10}{}^{*}\beta_{q,n,m} - \Delta z^{2}D = \log_{10}{}^{*}\beta_{q,n,m}^{0} - \Delta \varepsilon I_{m}$$
(12)

where

$$\Delta z^2 = z_{BaEDTA}^2 - z_{Ba}^2 - z_{EDTA}^2 = -16$$
(59)



Figure 5 – Extrapolation of BaEDTA<sup>2-</sup> stability constant to zero ionic strength using the SIT methodology. The  $2\sigma$  confidence bounds of the fit are the dotted lines and the uncertainties correspond to standard deviation obtained from the linear regressions of the apparent stability constants and from the uncertainties of the sodium-EDTA constants.

As it can be observed from figure 5, the linear fit is good for the data set, suggesting that the experimental data fits the theoretical model accurately. The intercept, i.e. (9.88±0.11), is equal to the stability constant of the BaEDTA<sup>2-</sup> complex formation at zero ionic strength. The uncertainties shown in figure 5 are largely originating from the standard deviations of the NaEDTA complex formation. As these standard deviations are quite large, especially for the higher ionic strengths, the standard deviations of the individual points and of the slope of the linear regression are affected to quite some extent. The ion interaction coefficient term,  $\Delta \varepsilon$ , is equal to the slope, with reversed sign, of the linear regression obtained by applying the SIT methodology to the data set. For the BaEDTA<sup>2-</sup> complex formation the ion interaction coefficient term is expressed as:

$$\Delta \varepsilon_{BaEDTA} = \varepsilon(BaEDTA^{2-}, Na^{+}) - \varepsilon(Ba^{2+}, Cl^{-}) + \varepsilon(EDTA^{4-}, Na^{+})$$
(60)

As the slope,  $\varepsilon(Ba^{2+},Cl^{-})$  and  $\varepsilon(EDTA^{4-},Na^{+})$  are all known, the ion interaction coefficient  $\varepsilon(BaEDTA^{2-},Na^{+})$  can be calculated as  $-(0.05\pm0.16)$ . The standard deviation of the linear fit, by ignoring the standard

deviations of the individual points, is equal to 0.03, which puts into perspective the influence of the propagated uncertainties of the NaEDTA constants.

#### 5.2.3 RaEDTA<sup>2-</sup> stability constant determination

At ionic strengths  $I_m$ =0.22, 0.50, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>) the plot of distribution ratios of <sup>226</sup>Ra against [H<sub>r</sub>EDTA<sup>(r-4)</sup>]<sub>tot</sub> is shown in figure. 6.



Figure 6 –Determination of apparent stability constants for RaEDTA<sup>2-</sup> in the linear regressions by least squares fitting at  $I_m$ =0.22, 0.50 (a), 1.02, 2.09 (b), and 2.64 (mol·kg<sup>-1</sup>) (c) according to Eq. (28). The  $2\sigma$  confidence bounds are the dotted lines and the uncertainties correspond to standard deviation based on duplicate samples.

The apparent stability constants determined in figure 6 are adjusted for the EDTA<sup>4-</sup> concentration in the same manner as for BaEDTA<sup>2-</sup> described in section 5.2.2. Applying the SIT methodology on the apparent stability constants allows for extrapolation to zero ionic strength, as well as for determination of the specific ion interaction coefficient term. The SIT extrapolation can be seen in figure 7.



Figure 7 - Extrapolation of RaEDTA<sup>2-</sup> stability constant to zero ionic strength using the SIT methodology. The  $2\sigma$  confidence bounds of the fit are the dotted lines and the uncertainties correspond to standard deviation obtained from the linear regressions of the apparent stability constants and from the uncertainties of the sodium-EDTA constants.

The large uncertainties of the data points shown in the linear regression in figure 7 are mostly originating from the uncertainty in the NaEDTA stability constants, as previously described in section 5.2.2. The stability constant of the RaEDTA complex formation can be seen as the intercept, equal to  $(9.11\pm0.09)$ . The slope is equal to the ion interaction coefficient term with reversed sign:

$$\Delta \varepsilon_{RaEDTA} = \varepsilon (RaEDTA^{2-}, Na^+) - \varepsilon (Ra^{2+}, Cl^-) + \varepsilon (EDTA^{4-}, Na^+)$$
(61)

As only the slope and the ion interaction coefficient  $\epsilon$ (EDTA<sup>4-</sup>,Na<sup>+</sup>) are known, the ion interaction coefficient  $\epsilon$ (RaEDTA<sup>2-</sup>,Na<sup>+</sup>) cannot be calculated, since the ion interaction coefficient  $\epsilon$ (Ra<sup>2+</sup>,Cl<sup>-</sup>) is unavailable in literature.

The practice of extrapolating alkaline earth metal data using the effective ionic radii in 8-fold coordination has been used by Langmuir and Riese to estimate the hydrolysis constant of radium [LAN85]. This procedure can also be applied to the ion interaction coefficients of the alkaline earth metal ions. The SIT ion interaction coefficients  $\epsilon(Mg^{2+},Cl^{-})$ ,  $\epsilon(Ca^{2+},Cl^{-})$  and  $\epsilon(Ba^{2+},Cl^{-})$  are reported by Ciavatta [CIA80], as

(0.19±0.02), (0.14±0.01) and (0.07±0.01) respectively. The effective ionic radii of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup> and Ra<sup>2+</sup> in 8-fold coordination, are reported by Shannon as 0.89, 1.12, 1.42 and 1.48 pm respectively [SHA76]. Linearly fitting the effective ionic radii in 8-fold coordination against the ion interaction coefficients for the alkaline earth metals makes it possible to extrapolate to the SIT ion interaction coefficient  $\epsilon$ (Ra<sup>2+</sup>,Cl<sup>-</sup>). The procedure can be seen in figure 8, resulting in  $\epsilon$ (Ra<sup>2+</sup>,Cl<sup>-</sup>)=(0.057±0.02). Using this estimation of the ion interaction coefficient, the  $\epsilon$ (RaEDTA<sup>2-</sup>,Na<sup>+</sup>) parameter can be calculated as –(0.16±0.15).



Figure 8 – Extrapolation of  $\varepsilon$ ( $Ra^{2+}$ ,  $Cl^{-}$ ) SIT ion interaction coefficient using ion interaction coefficients of other alkaline metals with their effective ionic radii [SHA76].

## 5.2.4 BaEDTA<sup>2-</sup> and BaEDTA<sup>2-</sup> stability constant comparison with literature data

A comparison of the determined metal-EDTA stability constants at zero ionic strength with available literature data is shown in table 7. The stability constants taken from literature were extrapolated to zero ionic strength using Davies equation [STU12], (using the additive term  $0.2 \cdot I_m$  instead of the, by Davies, originally proposed value of  $0.3 \cdot I_m$  [DAV62]).

Method	Metal ion	Ionic medium	Temperature (°C)	Reported $log_{10}\beta$	Extrapolated to zero ionic strength $\log_{10}\beta^0$	Reference
Ion exchange	Ba <sup>2+</sup>	0.2; 0.5; 1; 2; 2.5 (NaCl)	25.1	Table 8	9.88±0.11	This work
Review	Ba <sup>2+</sup>	0.1	25	7.86	9.64	Smith and Martell [MAR74]
рН	Ba <sup>2+</sup>	0.1 (KCl)	20	7.76	9.54	Schwarzen bach et al [SCH47]
pН	Ba <sup>2+</sup>	0	25	7.73	7.73	Carini et al[CAR54]
рН	Ba <sup>2+</sup>	0.1	25	7.9	9.68	Schmid et al [SCH56]
Ion exchange	Ba <sup>2+</sup>	0	25	9.92	9.92	Astakhov and Fomenko [AST57]
рН	Ba <sup>2+</sup>	0.1 (KNO <sub>3</sub> )	25	7.63	9.41	Bohigian et al [BOH60]
Paper electropho resis	Ba <sup>2+</sup>	0.1 (KNO <sub>3</sub> )	20	8	9.78	Jokl et al[JOK65]
рН	Ba <sup>2+</sup>	0.1 (KNO <sub>3</sub> or (CH <sub>3</sub> ) <sub>4</sub> N(NO <sub>3</sub> ))	25	7.8	9.58	Delgado et al [DEL82]
Ion exchange	Ra <sup>2+</sup>	0.2; 0.5; 1; 2; 2.5 M (NaCl)	25.1	Table 8	9.11±0.09	This work
Ion exchange	Ra <sup>2+</sup>	0.1 M <sup>b</sup>	20 <sup>b</sup>	7.12	8.9	Nikolsky et al [NIK59]
Ion exchange	Ra <sup>2+</sup>	0.1 M (sodium salt) <sup>c</sup>	20	7.07°	9.22°	Baetsle and Bengsch [BAE62]
Ion exchange	Ra <sup>2+</sup>	0.1 M (NaClO <sub>4</sub> )	25	7.7	9.29	Sekine et al [SEK68]
Estimated	Ra <sup>2+</sup>	0.1	25	7.4	9.2	Nelson et al [NEL60]

Table 7 - Comparison of reported stability constants for the formation of BaEDTA and RaEDTA

<sup>b</sup> ionic strength and temperature were assumed, <sup>c</sup> contribution of the 0.01 mol·l<sup>-1</sup> EDTA to the total ionic strength has been taken into account

As can be seen from the data in table 7, there is a very small variation in ionic strengths used to determine the stability constants. Without the data presented in this work, where stability constants are determined several ionic strengths, including high ionic strengths, it would be impossible to determine ion interaction coefficients, or ionic strength dependence of the stability constants. The extrapolation of the literature data shown in table 7 to zero ionic strength is in good agreement with the value determined in the present work, except for the value from Carini et al. [CAR54]. Consequently, this latter value is therefore disregarded.

Radium-EDTA complex formation has been studied previously by several researchers using both solvent extraction and ion exchange methods. The experimental data from these studies have been reviewed [AND13]. The first to study the RaEDTA<sup>2-</sup> complex formation was Nikolsky et. al. who obtained a log<sub>10</sub>K value of 7.12 [NIK59], which value was extrapolated to zero ionic strength from the presumed ionic strength and temperature 0.1 mol·1<sup>-1</sup> and 20 °C respectively. This complex formation has also been studied by Baetsle and Bengsch who used the Amberlite IR120 ion exchange resin at ionic strength 0.1 mol·1<sup>-1</sup> at 20 °C and reported the log<sub>10</sub>K value as 7.07±0.06 [BAE62]. When studying the complex formation, an EDTA<sup>4-</sup> concentration of 0.01 mol·l<sup>-1</sup> with acetate buffer was used. As this EDTA<sup>4-</sup> concentration has a significant contribution to the ionic strength which was not accounted for, the ionic strength was recalculated as 0.19  $mol \cdot l^{-1}$  before extrapolating to the value at zero ionic strength. Sekine et. al. used the solvent extraction method using a 0.1 M tributylphosphate and 0.1 M thenovltrifluoroacetone in CCl<sub>4</sub> solution to study the complex formation between Ra<sup>2+</sup> in conjunction with different aminocarboxylic acids in 0.1 mol·l<sup>-1</sup> NaClO<sub>4</sub> at 25 °C. The log<sub>10</sub>K value for RaEDTA<sup>2-</sup> was obtained as 7.7 [SEK68]. Nelson and co-workers estimated the stability constant for the RaEDTA<sup>2-</sup> complex as log<sub>10</sub>K=7.4 at ionic strength 0.1 mol·l<sup>-1</sup> and 25 °C [NEL60]. The obtained stability constant in this work for RaEDTA<sup>2-</sup> is in excellent agreement with the literature data shown in table 7, when taking ionic strength, temperature differences and other factors involved in the analysis of literature data (e.g. ionic strength corrections for EDTA<sup>4-</sup> concentration) into account. The value obtained by Sekine et. al. is most likely the best value to compare with the stability constants obtained in this work. Comparing these values at zero ionic strength gives a very good agreement.

All stability constants determined in this work for the MEDTA<sup>2-</sup> complex formation are shown in table 8.

$I_m (mol \cdot kg^{-1})$	$log_{10}\beta_{RaEDTA}$	$log_{10}\beta_{BaEDTA}$
0.00	(9.11±0.09)	$(9.88\pm0.11)$
0.22	$(6.98 \pm 0.08)$	$(7.61\pm0.08)$
0.51	(6.71±0.10)	$(7.32\pm0.10)$
1.02	$(6.37\pm0.11)^{a}$	$(7.00\pm0.11)$
2.09	(6.36±0.15)	$(7.02\pm0.14)$
2.64	(6.50±0.18)	$(6.99 \pm 0.18)$

Table 8 - Stability constants for MEDTA<sup>2-</sup> in NaCl at I<sub>m</sub>=0, 0.22, 0.51, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>).

<sup>a</sup> The ionic strength was slightly different, I<sub>m</sub>=1.03 (mol·kg<sup>-1</sup>)

The  $log_{10}\beta^{0}_{MEDTA}$  stability constants determined in this work can also be compared to stability constants of other alkaline earth metals at infinite dilution. The stability constant for the CaEDTA<sup>2-</sup> species formation is recommended through an extensive data review by OECD NEA [NEA05], as  $log_{10}\beta^{0}$ =(12.69±0.06). Least squares fitting of the  $log_{10}\beta^{0}_{MEDTA}$  stability constants against the effective ionic radii in 8-fold coordination yields a fit with r<sup>2</sup>=0.998, suggesting that the  $log_{10}\beta^{0}_{MEDTA}$  stability constants provided in this work are in good agreement with the literature data. The linear fit can be seen in figure 8. It is important to note that

 $Mg^{2+}$  cannot be compared to  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$  and  $Ra^{2+}$  in regard to its EDTA complex formation, as  $Mg^{2+}$  has a smaller ionic radius than  $Ca^{2+}$ , but still forms a weaker complex. The MgEDTA<sup>2-</sup> complex having a smaller stability constant might be due to steric hindrance, as the radius might be too small for the six donor groups of EDTA to be able to fit around the metal ion efficiently.

There are few reported stability constants for the SrEDTA<sup>2-</sup> complex formation in literature. The stability constants for the complex formation of SrEDTA<sup>2-</sup> as well as CaEDTA<sup>2-</sup> were determined by Felmy at infinite dilution and at 22-23°C as  $log_{10}\beta^0=10.45$  and  $log_{10}\beta^0=12.36$  respectively [FEL03]. The value for the CaEDTA<sup>2-</sup> complex formation determined by Felmy is significantly different from the value recommended by OECD NEA in their review [NEA05]. Interpolating between the  $log_{10}\beta^0_{MEDTA}$  stability constants determined in this work and the, by OECD NEA, recommended value for of  $log_{10}\beta^0_{CaEDTA}$  recommended by [NEA05], to the effective ionic radii in 8-fold coordination of Sr<sup>2+</sup>, the constant for the SrEDTA<sup>2-</sup> can be estimated as  $log_{10}\beta^0_{SrEDTA}=(11.36\pm0.19)$ , the procedure can be seen in figure 8. This value is considerably different from the value determined by Felmy.



Figure 9 – Least squares fit of the literature data for the stability constant of the [CaEDTA]<sup>2-</sup> complex recommended by [NEA05], and the stability constants of the [BaEDTA]<sup>2-</sup> and [RaEDTA]<sup>2-</sup> complexes determined in this work.

## 5.2.5 Study of Ba<sup>2+</sup>+HEDTA<sup>3-</sup> equilibrium

The hydrogen concentration was adjusted to maximize the molar fraction of the HEDTA<sup>3-</sup> form in order to study this complexation while minimizing the influences of the other EDTA forms. As can be seen in the speciation curve in figure 2, there is a broad region around  $-log_{10}[H^+]=8$  where there is a very high molar fraction of HEDTA<sup>3-</sup>. There is however small fractions of H<sub>2</sub>EDTA<sup>2-</sup> and EDTA<sup>4-</sup> present around this region. The H<sub>2</sub>EDTA<sup>2-</sup> form is expected to form comparatively very weak complexes and is therefore neglected as complexing agent. The  $-log_{10}[H^+]$  value at which the HEDTA<sup>3-</sup> molar fraction is optimized, is different at every ionic strength, since the pKa values are themselves dependent on ionic strength. The  $-log_{10}[H^+]$  values can be seen together with the relevant molar fractions in table 9.

	$I_m$ (mol·kg <sup>-1</sup> )	$-\log_{10}[H^+]$	$x_{EDTA^{4-}}$	$x_{HEDTA^{3-}}$
	0.22	8.0	5.65·10 <sup>-3</sup>	0.983
	0.51	7.9	6.04·10 <sup>-3</sup>	0.983
	1.02	7.9	5.45·10 <sup>-3</sup>	0.983
	2.09	8.2	3.58.10-3	0.985
_	2.64	8.3	$4.83 \cdot 10^{-3}$	0.984

Table 9 – Molar fractions of the different  $H_{(r-1)}EDTA^{(r-5)}$  forms in the different ionic strength sample series.

Even though the  $-\log_{10}[H^+]$  values are slightly different at the different ionic strengths, the speciation is very similar with respect to the molar fractions of the different H<sub>r</sub>EDTA<sup>(r-4)</sup> forms. As long as the molar fractions are known, the system can be accurately described. The apparent stability constants for the BaHEDTA<sup>-</sup> and complexes were derived from the experiments conducted at  $-\log[H^+]$  of 7.9-8.3 with mole fraction of HEDTA<sup>3-</sup>  $\geq$ 98% using the same method as for BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes and assuming formation of only BaHEDTA<sup>-</sup> according to the reaction shown in Eq. (18) where r=1. At ionic strengths  $I_m$ =0.22, 0.50, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>) the distribution ratios of <sup>133</sup>Ba are plotted against [H<sub>r</sub>EDTA<sup>(r-4)</sup>]<sub>tot</sub> in figure 10.



Figure 10 – Determination of apparent stability constants for  $Ba^{2+} + HEDTA^{-}$  equilibrium in the linear regressions by least squares fitting at  $I_m=0.22$ , 0.50 (a), 1.02, 2.09 (b), and 2.64 (mol·kg<sup>-1</sup>) (c) according to Eq. (28). The  $2\sigma$  confidence bounds are the dotted lines and the uncertainties correspond to standard deviation based on duplicate samples.

As the HEDTA<sup>3-</sup> fraction is dominant, the formation of NaHEDTA<sup>2-</sup> has to be taken into account when the HEDTA<sup>-</sup> stability constants are determined. A few experimental data for the NaHEDTA<sup>2-</sup> complex stability constant are available in literature. The stability constants at zero ionic strength,  $log_{10}K^0$ , vary greatly between 0.0 to 1.5 [PAL63][BOT65][DAN85][SAL91]. The most probable reason for the  $log_{10}K^\circ$  data inconsistencies is that the NaHEDTA<sup>2-</sup> complex is very weak, which makes it difficult to accurately distinguish the effects of complex formation in comparison to activity coefficient changes. This as well as other challenges related with the determination of stability constants of weak complexes have previously been discussed in detail [DAN08][MAR06]. The most reasonable value for the stability constant of
NaHEDTA<sup>2-</sup> complex is conceivably the value stated by Palaty [PAL63]. Temperature was not given by the author [PAL63], but based on all obtained values, it can be assumed that Na-EDTA equilibrium was studied at 25 °C. The author used ion selective electrodes to study EDTA dissociation and Na-EDTA equilibrium and obtained values that are in good agreement with the values listed in table 5 and table 6. Tetramethylammonium chloride was used as a background electrolyte and the total ionic strengths was 0.12 (mol·1<sup>-1</sup>). The reported stability constant at zero ionic strength for the NaHEDTA<sup>2-</sup> complex was  $log_{10}K^{\circ}$ =-0.03. The reported value by Palaty is subject to some uncertainty and it can be assumed that the actual  $log_{10}K^{\circ}$  value at zero ionic strength is in the range of -0.5 to 0.5 (i.e.  $log_{10}K^{0}$ =(0.0±0.5)). Presumably, the ascription of such a high uncertainty for the stability constant of this weak complex is the only way to overcome the lack of reliable data. The proposed uncertainty is in agreement with Marcus and Hefter who stated that for weak complex formation, the accuracy of the constant is difficult to estimate by experiments or theoretical approximations [MAR06].

To be able to extrapolate the NaHEDTA<sup>2-</sup>  $\log_{10}K^{\circ}$  value of (0.0±0.5) to the ionic strengths used in this work, it is important to know the SIT interaction parameters:  $\epsilon(Na^+, Cl^-)$ ,  $\epsilon(Na^+, HEDTA^{3-})$  and  $\epsilon(Na^+, NaHEDTA^{2-})$ . The first two parameters and their associated uncertainties are available in literature [GUI03][HUM05], and the last parameter has never been reported. Comparison of sodium SIT ion interaction coefficients with numerous different anionic ligands shows that this parameter typically varies between -0.3 to 0.1 [GUI03]. Furthermore, the sodium SIT interaction coefficients with ligands similar to H<sub>2</sub>EDTA<sup>2-</sup> is –(0.37±0.14) [HUM05]. Based on these values, the  $\epsilon(Na^+, NaHEDTA^{2-})$  SIT parameter has therefore been estimated as -(0.2±0.3) kg·mol<sup>-1</sup>, where a substantial uncertainty has been assigned. All the coefficients associated with NaHEDTA<sup>2-</sup> complexation (Eq. 37) that are necessary in this work are listed in table 10.

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	Parameter	Value	Reference				
	$\log_{10} K^{\circ}$	(0±0.5)	Estimated in this work, based on available experimental data from Palaty [PAL63]				
	ε(Na <sup>+</sup> ,Cl <sup>−</sup> )	$(0.03 \pm 0.01)$	Guillaumont et al. [GUI03]				
	ε(Na <sup>+</sup> ,HEDTA <sup>3-</sup> )	-(0.1±0.14)	Hummel et al. [HUM05]				
	ε(Na <sup>+</sup> ,NaHEDTA <sup>2-</sup> )	$-(0.2 \pm 0.3)$	Estimated in this work				

Table 10. Stability constants and SIT ion interaction parameters for the NaHEDTA<sup>2-</sup> complex formation (Eq. 37) at 25 °C

Assuming that the BaHEDTA<sup>-</sup> complex is the complex causing the redistribution of the Ba<sup>2</sup> ions, the SIT methodology can be applied to the apparent stability constants determined. The resulting linear regression can be seen in figure 11.



Figure 11 –Determination of apparent stability constants for  $Ba^{2+}$ +HEDTA<sup>3-</sup> = BaHEDTA<sup>-</sup> equilibrium in the linear regressions by least squares fitting at  $I_m$ =0.22, 0.50 (a), 1.02, 2.09 (b), and 2.64 (mol·kg<sup>-1</sup>) (c) according to Eq. (28). The  $2\sigma$  confidence bounds are the dotted lines and the uncertainties correspond to standard deviation based on duplicate samples.

The uncertainties are originating almost entirely from the large uncertainty assigned to the NaHEDTA<sup>2-</sup> complex formation constant. The determined apparent stability constants were extrapolated to zero ionic strength using the SIT method, which is the linear regression shown in figure 11, resulting in  $\log_{10}K^0$ =(7.04±0.12) for BaHEDTA<sup>-</sup> As this stability constant of BaHEDTA<sup>-</sup> at zero ionic strength is considerably lower the than the one for BaEDTA<sup>2-</sup> it is reasonable to assume that the stability constant for BaH<sub>2</sub>EDTA would be considerably lower than the BaHEDTA<sup>-</sup>. Using the slope received from the linear regression of the apparent stability constants, supposing that it is the BaHEDTA<sup>-</sup> complex that is studied, the ion interaction coefficient  $\epsilon$ (BaHEDTA<sup>-</sup>,Na<sup>+</sup>) can be calculated through:

$$\Delta \varepsilon_{BaHEDTA} = \varepsilon (BaHEDTA^{-}, Na^{+}) - \varepsilon (Ba^{2+}, Cl^{-}) + \varepsilon (HEDTA^{3-}, Na^{+})$$
(62)

which yields – $(0.20\pm0.16)$ . It is unreasonable that the ion interaction coefficient  $\epsilon$ (BaHEDTA<sup>-</sup>,Na<sup>+</sup>) would have a more negative value than  $\epsilon$ (BaEDTA<sup>2-</sup>,Na<sup>+</sup>), as the charge is lower. The BaHEDTA<sup>-</sup> complex has been studied by Schwarzenbach and Ackermann at ionic strength 0.1 mol·1<sup>-1</sup> and temperature 20 °C, resulting in the stability constant 2.07 [SCH47]. Extrapolating this value to zero ionic strength using Davies equation [STU12], results in the stability constant  $\log_{10} K^0=3.15$ , which can be compared to the stability constant obtained in this work. The value obtained in this study is four orders of magnitude greater than the constant provided by Schwarzenbach and Ackerman [SCH47]. This disparity has two likely explanations, either the stability constant determined by Schwarzenbach and Ackerman is inconsistent with other data, or it is not the BaHEDTA<sup>-</sup> complex that is formed according to Eq. (18), where r=1, as  $log_{10}[H^+]$  is in the range of 7.9-8.3. In order to check the former hypothesis, the data provided by Schwarzenbach and Ackermann can be compared with literature data where stability constants of EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> with various metals has been studied [MAR74][SCH54]. Comparing constants obtained under the same experimental conditions, a linear Gibbs free energy analysis, i.e. a plot of stability constants for a variety of metal ions with charge n  $\geq$ 2 together with EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> according to Eq. (18), can be performed, which is shown in figure 12.



Figure 12 – Linear free Gibbs energy analysis of the  $M^{n+}$ +EDTA<sup>4</sup> stability constants against the  $M^{n+}$ +HEDTA<sup>3-</sup> stability constants. The coefficient of determination shows quite a clear relation.

As can be seen in figure 12, there is a clear relation between the stability constant  $\beta_{ML}$  and  $\beta_{MHL}$ . According to this relation, it is evident that the stability constants  $\log_{10}\beta_{MHL}^0$  should be in the range of 2-3, for the Ba<sup>2+</sup> and Ra<sup>2+</sup> complexes (see Appendix A for more detailed values). This therefore strongly indicates the unlikelihood that the BaHEDTA<sup>-</sup> complex is the one studied by the distribution ratio method. These remarks suggest that the complex formation reaction that is studied through the ion exchange distribution experiment is not the one expected. This means that the reaction in Eq. (63):

$$Ba^{2+} + HEDTA^{3-} \rightleftharpoons BaHEDTA^{-} \tag{63}$$

is most likely not what results in the redistribution of the  $Ba^{2+}$  ions. As previously discussed, the HEDTA<sup>-</sup> is the dominant form of EDTA<sup>4-</sup>, which means that the redistribution of  $Ba^{2+}$  does occur by a complex formation with HEDTA<sup>3-</sup>. If these assumptions are correct, then it can be hypothesized that the following equilibrium occurred instead of previously proposed (63):

$$Ba^{2+} + HEDTA^{3-} \rightleftharpoons BaEDTA^{2-} + H^+ \tag{64}$$

with stability constant:

$$\beta_{BaEDTA+H} = \frac{[BaEDTA^{2-}][H^+]}{[Ba^{2+}][HEDTA^{3-}]}$$
(65)

The assumption that the reaction that has been studied in the one defined in Eq. (64) has to be motivated thoroughly. The redistribution of barium using the ion exchange method only takes the ligand and barium concentrations into account, i.e. the acid dissociation of the ligand during the complex formation reaction cannot be appropriately taken into account by the redistribution method only. According to Eq. (65), the apparent stability constants  $\beta_{BaEDTA+H}$  are equal to the apparent stability constants determined using the distribution ratio method, and subsequently corrected for the ionic media ligand complex formation, multiplied by the hydrogen concentration. The recalculated apparent stability constants for the BaEDTA<sup>2-</sup>+H<sup>+</sup> complex formation reaction can be seen in table 11.

Table 11 – Apparent stability constants determined according to the reaction shown in Eq. (65).

$I_m (mol \cdot kg^{-1})$	$log_{10}\beta_{BaEDTA+H}$
0.00	-(1.41±0.12)
0.22	-(2.63±0.06)
0.51	-(2.80±0.08)
1.02	-(3.21±0.08)
2.09	-(3.49±0.08)
2.64	-(3.75±0.08)

Using the SIT methodology, the stability constant at zero ionic strength for the equilibrium shown in Eq. (64) is calculated as  $\log_{10}\beta^0$ =-(1.41±0.12), with a slope of (0.14±0.08). The ion interaction coefficient  $\epsilon_2$ (BaEDTA<sup>2-</sup>,Na<sup>+</sup>) can therefore be calculated as -(0.01±0.16), and is in good agreement with the value determined for the BaEDTA<sup>2-</sup> complex in section 5.2.2. The SIT linear regression applied to the apparent stability constants given in table 11 is shown in figure 13.



Figure 13 - Extrapolation of stability constants of BaEDTA<sup>2</sup>+H<sup>+</sup> = BaEDTA + H equilibrium to zero ionic strength using SIT.

It could be worth mentioning that the coefficient of determination is not very indicative of the accuracy of the fit for low slopes, as the one shown in figure 13, because of the mathematical properties of  $r^2$  are such that it is equal to zero for a slope of zero [MIL02]. The stability constants for the suggested reaction shown in Eq. (64) can also be expressed through definitions of other stability constants in the specified experimental system:

$$\beta_{BaEDTA+H} = \frac{[BaEDTA^{2-}][H^+]}{[Ba^{2+}][HEDTA^{3-}]} = \frac{\beta_{BaEDTA}[Ba^{2+}][EDTA^{4-}][H^+]}{[Ba^{2+}][HEDTA^{3-}]} = \beta_{BaEDTA} \cdot K_{a,1}$$
(66)

Using the previously determined stability constant  $log_{10}\beta^0_{BaEDTA}$ , the stability constant  $log_{10}\beta^0_{BaEDTA+H}$  at zero ionic strength can be calculated as -(1.36±0.13). This is in good agreement with the stability constant determined, which is strong evidence for the occurrence of reaction (64) under the studied experimental conditions.

### 5.2.6 RaHEDTA<sup>-</sup> stability constant determination

At ionic strengths  $I_m$ =0.22, 0.50, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>) the distribution ratios of <sup>226</sup>Ra are plotted against [H<sub>r</sub>EDTA<sup>(r-4)</sup>]<sub>tot</sub> according to Eq. (28) in figure 14.



Figure 14 – Determination of apparent stability constants for  $Ra^{2+}$ +HEDTA<sup>3-</sup> equilibrium in the linear regressions by least squares fitting at  $I_m$ =0.22, 0.50 (a), 1.02, 2.09 (b), and 2.64 (mol·kg<sup>-1</sup>) (c) according to Eq. (28). The 2 $\sigma$  confidence bounds are the dotted lines and the uncertainties correspond to standard deviation based on duplicate samples.

Since the complex formation between Ba<sup>2+</sup> and HEDTA<sup>3-</sup> did not mainly form the complex BaHEDTA<sup>-</sup>, it is highly unlikely that the RaHEDTA<sup>-</sup> complex is formed under identical experimental conditions, with the only exception that the metal ion is replaced by Ra<sup>2+</sup>, because of the very similar chemistry of these two alkaline earth metal ions in solution. As the apparent stability constants obtained from the BaHEDTA<sup>-</sup> analysis could easily be converted into the constants describing the highly likely occurring reaction shown in Eq. (64), the SIT methodology is also here applied to the data received from the distribution ratio experimental data shown in figure 14. The linear regression of the applied SIT methodology is shown in figure 15.



Figure 15 – Determination of apparent stability constants for  $Ba^{2+}$ +HEDT<sup>3-</sup>=BaHEDTA<sup>-</sup> equilibrium in the linear regressions by least squares fitting at  $I_m$ =0.22, 0.50 (a), 1.02, 2.09 (b), and 2.64 (mol·kg<sup>-1</sup>) (c) according to Eq. (28). The 2 $\sigma$  confidence bounds of the fit are the dotted lines and the uncertainties correspond to standard deviation based on duplicate samples.

The radium stability constant for the redistribution of radium between the aqueous phase and the resin phase is, as discussed in the previous section, is not for the RaHEDTA<sup>-</sup> complex. The redistribution therefore occurs through:

$$Ra^{2+} + HEDTA^{3-} \rightleftharpoons RaEDTA^{2-} + H^+ \tag{67}$$

with stability constant:

$$\beta_{Ra+HEDTA} = \frac{[RaEDTA^{2-}][H^+]}{[Ra^{2+}][HEDTA^{3-}]}$$
(68)

Multiplying the apparent stability constants established by the distribution ratio linear regressions at ionic strengths  $I_m$ =0.22, 0.50, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>) by the hydrogen concentrations yields the corresponding stability constants for the reaction shown in Eq. (67). The recalculated stability constants can be applied to the SIT methodology (identical to the procedure in the previous section) which makes it possible to extrapolate to zero ionic strength. The linear regression can be seen in figure 16.



Figure  $16 - Extrapolation of stability constants of Ra^{2+} + HEDTA^{3-} = RaEDTA^{2-} + H^+ equilibrium to zero ionic strength using SIT.$ 

The slope of the linear regression shown in figure 16 is equal to  $-(0.10\pm0.07)$ , which makes it possible to calculate the ion interaction coefficient  $\epsilon_2(\text{RaEDTA}^2,\text{Na}^+)=-(0.06\pm0.16)$ , using the linearly estimated coefficient for  $\epsilon(\text{Ra}^{2+},\text{Cl}^-)$ . This is in good agreement with the previously determined ion interaction coefficient in section 5.2.3. The reason for the quite low coefficient of determination in figure 16 is mainly the low slope as previously discussed.

The stability constant  $\beta_{RaEDTA+H}$  can equivalently be calculated through  $\beta_{RaEDTA}$ . K<sub>a</sub>, as shown in section 5.2.5, which gives the stability constant  $\log_{10}\beta_{RaH}$ =-(2.13±0.12) at zero ionic strength. This is in good agreement with the data obtained applying the SIT methodology to the recalculated apparent stability constants. The stability constants for the reactions occurring in the lower  $-\log_{10}[H^+]$  region are summed up in table 12. The differences between the stability constants are very similar to the data obtained in the EDTA<sup>4-</sup> complex formation sections, suggesting that the two sets of experiments are in agreement.

$I_m (mol \cdot kg^{-1})$	$log_{10}\beta_{RaEDTA+H}$	$log_{10}\beta_{BaEDTA+H}$
0.00	-(2.07±0.11)	-(1.41±0.12)
0.22	-(3.26±0.06)	-(2.63±0.06)
0.51	-(3.42±0.08)	-(2.80±0.08)
1.02	$-(3.85\pm0.08)^{b}$	-(3.21±0.08)
2.09	-(4.15±0.10)	-(3.49±0.08)
2.64	-(4.24±0.08)	-(3.75±0.08)

Table 12 – Stability constants of reaction (64) determined by recalculating the apparent stability constants determined by the distribution ratio calculations.

The importance of the Na+HrEDTA<sup>(r-4)</sup> complex formation was under all experimental conditions of significant magnitude. The comparison of the apparent stability constants with and without taking the sodium effect into account is shown in tables 13 and 14 below.

Table 13 – Apparent stability constants at ionic strengths  $I_m=0.22, 0.51, 1.02, 2.09$  and 2.64 (mol·kg<sup>-1</sup>) without the sodium ligand interaction taken into account.

$I_m (\mathrm{mol}\cdot\mathrm{kg}^{-1})$	$log_{10}\beta_{RaEDTA}$	$log_{10}\beta_{RaEDTA+H}$	$log_{10}eta_{BaEDTA}$	$log_{10}eta_{BaEDTA+H}$				
0.22	(5.89±0.11)	-(3.29±0.14)	(6.63±0.06)	-(2.58±0.12)				
0.51	(5.41±0.08)	-(3.44±0.20)	(6.14±0.06)	-(2.73±0.20)				
1.02	(5.05±0.23) <sup>b</sup>	-(3.90±0.15)	(5.58±0.15)	-(3.20±0.09)				
2.09	(4.82±0.13)	-(4.19±0.09)	(5.34±0.13)	-(3.46±0.21)				
2.64	(4.68±0.15)	-(4.19±0.22)	(5.21±0.09)	-(3.73±0.09)				
<sup>b</sup> The ionic strength was slightly different, $I_m$ =1.03 (mol·kg <sup>-1</sup> )								

Table 14 - Sodium-EDTA corrected apparent stability constants in NaCl at ionic strengths  $I_m$ =0.22, 0.51, 1.02, 2.09 and 2.64 (mol·kg<sup>-1</sup>).

$I_m (mol \cdot kg^{-1})$	$log_{10}\beta_{RaEDTA}$	$log_{10}\beta_{RaEDTA+H}$	$log_{10}\beta_{BaEDTA}$	$log_{10}\beta_{BaEDTA+H}$
0.22	(6.97±0.11)	-(3.19±0.14)	(7.74±0.06)	-(2.52±0.12)
0.51	$(6.69 \pm 0.08)$	-(3.32±0.20)	$(7.40\pm0.06)$	-(2.68±0.20)
1.02	(6.49±0.23) <sup>b</sup>	-(3.71±0.15) <sup>b</sup>	(7.05±0.15)	-(3.15±0.09)
2.09	(6.63±0.13)	-(3.94±0.09)	(7.17±0.13)	-(3.32±0.21)
2.64	(6.67±0.15)	-(3.90±0.22)	(7.22±0.09)	-(3.58±0.09)
<sup>b</sup> The	ionic strength	was slightly diffe	rent I_=1 03 (n	$nol k\sigma^{-1}$

The ionic strength was slightly different,  $I_m = 1.03 \text{ (mol·kg}^{-1})$ 

As is shown in tables 13 and 14, the sodium-EDTA correction was not as significant for the HEDTA<sup>3-</sup> cases, as would be expected from the much lower equilibrium constant for this complex formation.

#### 5.3 Specific ion interaction coefficients

The SIT ion interaction coefficient terms were solved for the ε(MH<sub>(r-n)</sub>EDTA<sup>(r-n-3)</sup>,Na<sup>+</sup>) interaction according to Eq. (14):

$$\Delta \varepsilon = \varepsilon(complex, N \text{ or } X) - q\varepsilon(N, L) - m\varepsilon(M, X) + n\varepsilon(H, X)$$
(14)

The ion interaction coefficients taken from literature and the ones established in this work can be found in table 15. The  $\epsilon$ (MH<sub>(r-n)</sub>EDTA<sup>(r-n-3)</sup>,Na<sup>+</sup>) SIT ion interaction coefficients are calculated using the estimated  $\varepsilon(Ra^{2+},Cl^{-})$  value.

Interaction	SIT coefficients	Reference
ε(H <sup>+</sup> ,Cl <sup>-</sup> )	(0.123±0.002)	This work <sup>a</sup>
ε(EDTA <sup>4-</sup> ,Na <sup>+</sup> )	(0.32±0.14)	NEA05
ε(HEDTA <sup>3-</sup> ,Na <sup>+</sup> )	-(0.10±0.14)	NEA05
$\epsilon(\mathrm{Ra}^{2+},\mathrm{Cl}^{-})$	(0.057±0.010)	This work <sup>b</sup>
$\epsilon(\mathrm{Ba}^{2+},\mathrm{Cl}^{-})$	$(0.07 \pm 0.01)$	CIA80
$\epsilon(Ca^{2+},Cl^{-})$	$(0.14 \pm 0.01)$	CIA80
$\epsilon(Mg^{2+},Cl^{-})$	(0.19±0.02)	CIA80
ε(MgEDTA <sup>2-</sup> ,Na <sup>+</sup> )	-(0.01±0.15)	CIA80
ε(RaEDTA <sup>2-</sup> ,Na <sup>+</sup> )	$-(0.10\pm0.11)^{d}$	This work
ε(BaEDTA <sup>2-</sup> ,Na <sup>+</sup> )	$-(0.03\pm0.11)^{d}$	This work
$\Delta \epsilon (RaEDTA^{2-})$	-(0.54±0.06)	This work
$\Delta \epsilon (RaEDTA^{2-}+H^{+})$	(0.10±0.07)	This work
$\Delta \epsilon (BaEDTA^{2})$	-(0.44±0.07)	This work
$\Delta \epsilon (BaEDTA^{2-}+H^{+})$	$(0.14 \pm 0.08)$	This work
$\Delta \epsilon$ (MgEDTA <sup>2-</sup> )	-(0.52±0.04)	NEA05
$\Delta \epsilon$ (CaEDTA <sup>2-</sup> )	-(0.50±0.50)	NEA05
ε(Na <sup>+</sup> ,NaHEDTA <sup>2-</sup> )	-(0.20±0.30)	This work <sup>c</sup>

Table <u>15 – SIT ion interaction coefficients established in this work and taken from literature</u>

<sup>a</sup> Calculated from titration curves made at 23±0.5°C, <sup>b</sup> Calculated by extrapolation of data from [CIA80], <sup>c</sup> Estimated from other reliable data found in literature and assigned a large uncertainty (see section 5.3), <sup>d</sup> Weighted means of the individual ion interaction coefficients determined in the two different pH-regions.

The terms for  $\Delta\epsilon(MgEDTA^{2-})$  and  $\Delta\epsilon(CaEDTA^{2-})$  are given by OECD NEA [NEA05] as  $-(0.52\pm0.04)$  and  $-(0.5\pm0.5)$  respectively. These correspond well with the SIT ion interaction coefficient terms established in this work,  $\Delta\epsilon(RaEDTA^{2-})$  and  $\Delta\epsilon(BaEDTA^{2-})$  equal to  $-(0.54\pm0.06)$  and  $-(0.44\pm0.07)$  respectively. All ion interaction parameters of radium and barium are similar, with the difference that radium has slightly lower  $\Delta\epsilon$ -terms and SIT ion interaction coefficients. The ion interaction coefficients for the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes were found to be in very good agreement between the two experimental data series conducted at  $-\log_{10}[H^+]$  in the range of 7.9-8.3 and  $-\log_{10}[H^+]\geq12.0$ . The very good correspondence between the two data sets suggest that the estimated ion interaction coefficients are accurate, as well as the used NaHEDTA<sup>2-</sup> equilibrium constant provided by Palaty [PAL63]. The correspondence also suggests that the experimental conditions.

# 6. Conclusion

The apparent stability constants of barium and radium EDTA complexes were determined over a wide range of NaCl concentrations (0.2-2.5 M) at  $-\log_{10}[H^+] \sim 8$  and 12.4 at 25 °C. Determined stability constants were then extrapolated to zero ionic strength using the SIT methodology. The determined stability constants and ion interaction coefficients are important for describing the dissolution of Ba(Ra)SO<sub>4</sub> co-precipitate using EDTA, especially at high ionic strengths.

pH has a considerable influence on the stability constants at zero ionic strength of complex formation between alkaline earth metals and EDTA. The stability constants at infinite dilution for the complex formed in the high pH region are  $log_{10}^*\beta^0_{Ba,0,1} = (9.88 \pm 0.11)$  and  $log_{10}^*\beta^0_{Ba,0,1} = (9.11 \pm 0.09)$ . These stability constants are in excellent agreement with values previously published in literature. As all previously experimentally determined stability constants were provided at low ionic strength, there was no possibility of calculating ion interaction coefficients. To the best of our knowledge, the ion interaction coefficient terms of radium were experimentally determined for the first time in this work:  $\Delta\epsilon(BaEDTA^{2-})=-(0.44\pm0.07)$  and  $\Delta \epsilon$ (RaEDTA<sup>2-</sup>)=-(0.54±0.06). This makes it possible to calculate the ion interaction coefficients  $\varepsilon$ (BaEDTA<sup>2-</sup>,Na<sup>+</sup>)=-(0.03±0.11) and  $\varepsilon$ (RaEDTA<sup>2-</sup>,Na<sup>+</sup>)=-(0.10±0.11). The BaEDTA<sup>2-</sup>+H<sup>+</sup> and RaEDTA<sup>2-</sup> +H<sup>+</sup> complex formation reactions have stability constants  $\log_{10} \beta^{0}_{BaEDTA+H}$ =-(1.41±0.12) and  $log_{10}^*\beta_{RaEDTA+H}^0$ =-(2.07±0.11). The proposed formation reactions fit the experimental data very accurately, providing ion interaction coefficients that are consistent with the ones determined in the high pH region. Thus, comparisons of the ion interaction coefficients, and therefore the ionic strength dependence of Ba<sup>2+</sup> and Ra<sup>2+</sup> in NaCl-EDTA<sup>4-</sup> systems can be performed. The difference in stability constants in log units between the MEDTA<sup>2-</sup> complex formation reactions is very similar to the corresponding difference between the M<sup>2+</sup>+HEDTA<sup>3-</sup> complex formation reactions. The difference in stability constants in log units between the MEDTA<sup>2-</sup> and the M<sup>2+</sup>+HEDTA<sup>3-</sup> reactions is also very similar between radium and barium, indicating that the differences between radium and barium complex formation are quite consistent between different experimental conditions. A comparison of the obtained values at zero ionic strength indicate that Ba<sup>2+</sup> and Ra<sup>2+</sup> complex formation with EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> is mostly electrostatic. The similarity of the barium and radium ion interaction parameters indicates that both metal ions undergo very similar short- and longrange electrostatic interactions with EDTA<sup>4-</sup> and Cl<sup>-</sup>. The results also show that using the SIT interaction parameters of Ba<sup>2+</sup> as a substitute for Ra<sup>2+</sup> SIT interaction parameters that are unavailable could be a potentially useful tool for the Ra<sup>2+</sup>-NaCl-EDTA<sup>4-</sup> system taking into account the uncertainties of associated ion interaction coefficients.

The distribution method can be a powerful tool for studying complex formation reactions occurring in the Ra<sup>2+</sup>/Ba<sup>2+</sup>-NaCl-EDTA<sup>4-</sup> systems. When investigating complex formations in Ra<sup>2+</sup>-Ba<sup>2+</sup>-Na-Cl systems, the use of the ion exchange resin method would be advocated for future experimental work as it effectively circumvents issues of working with substantial amounts of radioactivity. It is also an effective method for studies at high ionic strength, making it useful for the determination of ion interaction coefficients.

# 7. Future work

There is in general a lack of radium thermodynamic properties and also organic ligand ion interaction coefficients, therefore determination of these could contribute to the understanding of their chemistry in solution. A thorough and precise determination of  $\varepsilon(Ra^{2+},Cl^{-})$  would also be useful for future complex formation reactions of alkaline earth metals in NaCl media. Complex formation reactions that would be interesting in future studies would for example be a precise determination of the ISA<sup>-</sup> complex formation with Ba<sup>2+</sup> and Ra<sup>2+</sup>, which would be relevant for repository conditions, as well as other particularly strong complex formation reactions with other organic complexing ligands, such as DOTA or cryptands.

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# Appendix A

## 1.1 Linear free Gibbs energy analysis

Linear free Gibbs energy analysis of the EDTA data used in figure 12, all data are taken from [SCH47], [SCH54], [MAR74].

Ion	$log_{10}\beta_{ML+H}$	$log_{10}\beta_{ML}$	$log_{10}\beta_{MHL}$
Mn2+	3.1	14.04	6.92
Co2+	3	16.31	9.09
Ni2+	3.2	18.62	11.6
Cu2+	3	18.8	11.58
Zn2+	3	16.5	9.28
Cd2+	2.9	16.46	9.14
Pb2+	2.8	18.04	10.62
VO2+	3	18.77	11.55
A13+	2.5	16.13	8.41
Sc3+	2	23.1	14.88
La3+	2	15.5	7.28
Nd3+	2	16.51	8.29
Fe3+	1.4	25.1	16.28
Ba2+		7.76	2.07
Ca2+		10.59	3.51
Mg2+		8.69	2.28
Be2+		8.4	2.1
Fe2+		14.33	6.86
Hg2+		21.8	14.6
Sr2+		8.63	2.3
Ga3+	1.91	20.5	12.19
In3+	1.5	25.3	16.58
Th4+	1.98	25.3	17.06
Cr2+	3	13.61	6.39
T13+	2.3	22.5	14.58

# 1.2 Distribution ratio series data

The distribution ratio	data for the Ba <sup>2-</sup>	and Ra <sup>2+</sup> in	EDTA <sup>4-</sup>	and HEDTA <sup>3-</sup>	regions are given in	the table.

I=0.2167	Batch 1	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	20.5306	1.1595	2.1971	1.2572
2	1.333E-05	46.3467	2.9519	5.2573	1.9075
3	2.000E-05	76.1011	3.7403	8.7853	2.0109
4	2.667E-05	114.2592	6.2890	12.6202	2.6135
5	3.333E-05	127.2629	10.5889	16.1165	2.6328
6	4.000E-05	119.9605	6.8498	21.0599	3.6916
7	4.667E-05	124.8759	8.8525	23.8773	4.2738
8	5.333E-05	210.2802	9.7357	28.9774	4.9424
9	6.000E-05	229.7309	16.7631	34.9176	4.5906
10	6.667E-05	281.8757	21.0621	42.3309	4.6063
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=0.2167	Batch 2	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	16.6456	0.9748	1.5890	1.1129
2	1.333E-05	40.5311	1.0759	4.1635	1.7341
3	2.000E-05	67.5354	2.7426	6.9261	1.8364
4	2.667E-05	97.0345	4.1932	9.6901	1.7534
5	3.333E-05	129.8813	6.3540	11.6158	2.6590
6	4.000E-05	157.0419	8.6763	12.7874	2.5837
7	4.667E-05	200.0555	10.5783	18.5605	3.6742
8	5.333E-05	199.9718	12.5334	21.1912	3.4856
9	6.000E-05	242.0072	14.1764	22.7836	4.1292
10	6.667E-05	312.0428	16.2699	30.7544	3.6723
11.1	0.000E+00	1.0000	1.0000	1.0000	1.0000
11.2	0.000E+00	1.0000	1.0000		
I=0.5062	Batch 1	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	7.1843	1.1438	1.3716	0.9278
2	1.333E-05	11.5188	1.5336	2.7488	1.1000
3	2.000E-05	25.2273	2.9293	8.9142	1.3619
4	2.667E-05	33.8739	3.7200	4.7650	1.6702
5	3.333E-05	47.6120	4.6756	7.4199	2.0818
6	4.000E-05	65.6664	5.5068	9.0000	1.6368
7	4.667E-05	65.1628	7.7173	11.0398	2.4391

8	5.333E-05	54.9357	9.0968	12.8360	1.9913
9	6.000E-05	81.7887	10.4642	14.4675	2.3808
10	6.667E-05	96.8871	12.1594	20.2054	2.4151
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=0.5062	Batch 2	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA <sup>-</sup>
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	5.1423	1.0034	1.1919	0.9596
2	1.333E-05	13.4881	1.0560	2.2522	1.1357
3	2.000E-05	22.8834	1.6908	3.5757	1.4973
4	2.667E-05	29.8631	2.3779	5.0615	2.1087
5	3.333E-05	41.0032	3.2434	6.5208	1.8179
6	4.000E-05	49.7427	4.2923	3.5979	1.9605
7	4.667E-05	75.9951	4.7422	9.2931	2.6643
8	5.333E-05	56.6856	5.9905	11.6418	2.4429
9	6.000E-05	78.2264	6.6068	13.5242	2.5827
10	6.667E-05	80.4681	7.7950	17.9011	3.9904
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=1.022	Batch 1	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA <sup>-</sup>
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	2.3229	0.9640	1.0958	0.9196
2	1.333E-05	4.6481	1.2437	1.5848	1.1362
3	2.000E-05	7.3118	1.7800	2.5498	1.3849
4	2.667E-05	11.5173	2.0371	3.2738	1.2701
5	3.333E-05	17.0387	1.9146	3.8386	1.2020
6	4.000E-05	12.3660	2.2056	5.0393	1.5122
7	4.667E-05	23.5462	4.2369	6.2991	1.3254
8	5.333E-05	25.7427	3.5611	6.7975	1.7286
9	6.000E-05	14.3129	3.3842	8.3471	1.5296
10	6.667E-05	20.0341	3.6276	9.2720	1.6645
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=1.022	Rotch 2	$\mathbf{D} \cdot \mathbf{E} \mathbf{D} \mathbf{T} \mathbf{A}^2$	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA <sup>-</sup>
	Daten 2	BaedIA	Durille	RalD17	Italie III
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
sample 1	[EDTA]tot 6.667E-06	lambda/D 1.9755	lambda/D 1.0429	lambda/D 0.7679	lambda/D 0.7365
sample 1 2	[EDTA]tot 6.667E-06 1.333E-05	lambda/D 1.9755 4.7208	lambda/D 1.0429 1.0564	lambda/D 0.7679 1.1052	lambda/D 0.7365 1.0782
sample 1 2 3	EDTA]tot 6.667E-06 1.333E-05 2.000E-05	BaEDTA <sup>-</sup> lambda/D 1.9755 4.7208 6.9126	lambda/D 1.0429 1.0564 1.3044	lambda/D 0.7679 1.1052 1.4607	lambda/D 0.7365 1.0782 1.0827
sample 1 2 3 4	[EDTA]tot 6.667E-06 1.333E-05 2.000E-05 2.667E-05	BaEDTA <sup>-</sup> lambda/D 1.9755 4.7208 6.9126 10.9204	lambda/D 1.0429 1.0564 1.3044 1.6029	lambda/D 0.7679 1.1052 1.4607 2.0282	lambda/D 0.7365 1.0782 1.0827 1.2640
sample 1 2 3 4 5	EDTA]tot 6.667E-06 1.333E-05 2.000E-05 2.667E-05 3.333E-05	BaEDTA <sup>-</sup> lambda/D 1.9755 4.7208 6.9126 10.9204 13.8806	lambda/D 1.0429 1.0564 1.3044 1.6029 2.0691	lambda/D 0.7679 1.1052 1.4607 2.0282 2.5384	lambda/D 0.7365 1.0782 1.0827 1.2640 1.2513
sample 1 2 3 4 5 6	EDTA]tot 6.667E-06 1.333E-05 2.000E-05 2.667E-05 3.333E-05 4.000E-05	BaEDTA <sup>-</sup> lambda/D 1.9755 4.7208 6.9126 10.9204 13.8806 17.0470	lambda/D 1.0429 1.0564 1.3044 1.6029 2.0691 2.4339	lambda/D 0.7679 1.1052 1.4607 2.0282 2.5384 3.3309	lambda/D 0.7365 1.0782 1.0827 1.2640 1.2513 1.7425

8	5.333E-05	21.3805	3.1518	4.1420	1.6283
9	6.000E-05	24.4810	3.6857	5.1458	1.5450
10	6.667E-05	29.5080	3.7346	5.8915	1.5719
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=2.086	Batch 1	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	1.5433	1.3029	1.0162	0.6899
2	1.333E-05	2.8414	1.3057	1.3436	0.7684
3	2.000E-05	4.4151	1.6853	1.3804	1.1164
4	2.667E-05	4.7412	2.0222	1.8928	1.0935
5	3.333E-05	6.7263	2.4672	2.5720	0.9199
6	4.000E-05	8.8915	3.1213	2.9138	1.2421
7	4.667E-05	9.1867	3.6563	3.2517	1.1181
8	5.333E-05	10.1936	3.6185	3.4064	1.6950
9	6.000E-05	15.2888	4.6324	3.6469	1.2351
10	6.667E-05	16.8184	4.9314	4.1739	1.5957
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=2.086	Batch 2	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	1.1245	1.0183	1.0444	0.6443
2	1.333E-05	2.1009	1.0179	1.2511	0.8658
3	2.000E-05	3.2678	1.1033	1.4611	0.9223
4	2.667E-05	4.5772	1.3449	1.9512	1.1182
5	3.333E-05	5.2632	1.6757	1.6055	1.0872
6	4.000E-05	6.4668	2.0589	3.1608	1.3161
7	4.667E-05	8.9140	2.4616	3.2122	1.1909
8	5.333E-05	11.3728	2.9421	3.6164	2.0440
9	6.000E-05	10.1061	3.2110	4.1211	1.4323
10	6.667E-05	12.2956	3.4458	6.7712	1.4247
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=2.637	Batch 1	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	1.2035	1.0271	1.3389	0.8709
2	1.333E-05	1.8997	1.0412	1.6212	0.8940
		2 0072	1.2456	1.5324	0.9804
3	2.000E-05	2.9072			
3 4	2.000E-05 2.667E-05	3.7169	1.5122	1.9808	0.8925
3 4 5	2.000E-05 2.667E-05 3.333E-05	3.7169 4.4337	1.5122 1.7546	1.9808 2.4917	0.8925 1.1528
3 4 5 6	2.000E-05 2.667E-05 3.333E-05 4.000E-05	2.9072 3.7169 4.4337 4.2557	1.5122 1.7546 1.9567	1.9808 2.4917 2.6408	0.8925 1.1528 1.2534

8	5.333E-05	8.2990	2.4345	3.2424	1.1891
9	6.000E-05	10.1383	3.1466	3.4840	1.6517
10	6.667E-05	13.0920	3.2552	4.7614	1.7178
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=2.637	Batch 2	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA <sup>-</sup>
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	1.2609	0.9964	1.0049	0.6452
2	1.333E-05	1.9045	1.0029	1.1552	1.0333
3	2.000E-05	2.9473	1.1028	1.2945	1.1993
4	2.667E-05	4.8366	1.3367	1.5559	1.1387
5	3.333E-05	4.3986	1.5885	1.9809	1.2636
6	4.000E-05	5.1674	1.9867	2.1513	1.1954
7	4.667E-05	6.2351	2.0736	2.5563	1.4042
8	5.333E-05	7.3293	2.3723	2.7621	1.6360
9	6.000E-05	9.5928	2.5807	3.3256	1.4180
10	6.667E-05	9.4371	2.8346	3.6181	1.8087
11	0.000E+00	1.0000	1.0000	1.0000	1.0000
I=0.2167	Batch 3	BaEDTA <sup>2-</sup>	BaHEDTA <sup>-</sup>	RaEDTA <sup>2-</sup>	RaHEDTA <sup>-</sup>
sample	[EDTA]tot	lambda/D	lambda/D	lambda/D	lambda/D
1	6.667E-06	21.2614		1.4227	
2	1.333E-05	46.0662		4.9781	
3	2.000E-05	71.2890		8.9405	
4	2.667E-05	97.7705		13.5867	
5	3.333E-05	113.9104		19.1125	
6	4.000E-05			25.3283	
7	4.667E-05			32.8719	
8	5.333E-05			38.5148	
9	6.000E-05			45.7098	
10	6.667E-05	242.1822		55.9473	
11	0.000E+00	1.0000		1.0000	

#### 1.3 Equilibrium time study

As the equilibration time of the complex formation is rather slow, the samples had to be shaken several times in order to speed up the equilibrium. As no shaking machine was available for the quite active samples, the shaking had to be done manually with some time in between the shakings. To illustrate the quite dramatic effect of the first few shakings, the cpm detected by LSC in the aqueous phase can be seen as a function of shakings.



Paper I

# Study of barium and radium complexation with ethylenediaminetetraacetic acid in aqueous alkaline sodium chloride media

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#### Abstract

The speciation of  $Ra^{2+}$  and  $Ba^{2+}$  with EDTA was investigated at 25 °C in aqueous alkaline NaCl media as a function of ionic strength (0.2 – 2.5 M) in two pH regions where the EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> species dominate. The stability constants for the formation of the [BaEDTA]<sup>2-</sup> and [RaEDTA]<sup>2-</sup> complexes were determined using an ion exchange method. Barium-133 and radium-226 were used as radiotracers and their concentrations in the aqueous phases were measured using liquid scintillation counting and gamma spectrometry, respectively. The specific ion interaction theory (SIT) was used to account for [NaEDTA]<sup>3-</sup> and [NaHEDTA]<sup>2-</sup> complex formation, and used to extrapolate the apparent stability constants to zero ionic strength (BaEDTA<sup>2-</sup>: 9.86 ± 0.09; RaEDTA<sup>2-</sup>: 9.13 ± 0.07) and obtain the Ba<sup>2+</sup> and Ra<sup>2+</sup> ion interaction parameters: ( $\epsilon(Na^+, BaEDTA^{2-})$ : -(0.03±0.11);  $\epsilon(Na^+, RaEDTA^{2-})$ : -(0.10±0.11)). It was found that in the pH region where HEDTA<sup>3-</sup> dominates, the reaction of Ba<sup>2+</sup> or Ra<sup>2+</sup> with the HEDTA<sup>3-</sup> ligand also results in the formation of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes (as it does in the region where the EDTA<sup>4-</sup> ligand dominates) with the release of a proton. Comparison of the ion interaction parameters of Ba<sup>2+</sup> and Ra<sup>2+</sup> strongly indicates that both metal ions and their EDTA complexes have similar activity coefficients and undergo similar short-range interactions in aqueous NaCl media.

**Keywords**: alkaline-earth metal, EDTA, complex formation, activity coefficient, specific ion interaction theory, infinite dilution

#### 1. Introduction

Barium and radium are members of the alkaline-earth metal group. While barium is an abundant element in the earth's crustal rocks (340 mg·kg<sup>-1</sup>), radium occurs in nature only in trace amounts (0.1 ng·kg<sup>-1</sup>) [1]. Radium has no stable isotopes and the most abundant radium isotope is <sup>226</sup>Ra with a half-life of 1600 years. Radium-226 is part of the <sup>238</sup>U decay chain and decays to the short lived ( $t_{1/2}$ =3.4 d)  $\alpha$ -emitting gas <sup>222</sup>Rn.

Both <sup>226</sup>Ra and <sup>222</sup>Rn are among the more radiotoxic elements present in the environment [2]. As a consequence of some anthropogenic processes, <sup>226</sup>Ra is concentrated in waste streams. For example, in uranium mining, uranium is usually leached from milled uranium ore or leached in situ using sulfuric acid. After leaching, the tailings (solid and liquid residues) are usually neutralized and disposed in surface ponds in the form of a slurry [3,4]. Predominantly, radium is rapidly dissolved in leaching and co-precipitates in the form of Ba(Ra)SO<sub>4</sub> [5]. The concentration of <sup>226</sup>Ra in such tailings is higher than in the natural uranium ore and can reach up to 43.4 kBq·kg<sup>-1</sup> (1186.7 ng·kg<sup>-1</sup>) [6]. The background radiation levels are also increased, mostly because of radium and its decay products, for example, from 0.1 - 0.2  $\mu$ Sv·h<sup>-1</sup> in reference areas such as the tailings storage facility up to 10-20  $\mu$ Sv·h<sup>-1</sup> on the top of waste dumps [6]. Radium-226 concentrations up to 200 Bq·l<sup>-1</sup> (0.2 nmol·l<sup>-1</sup>) also occur in water produced from the petroleum industry, which is above the limits of industrial effluents [7]. Radium-226 is usually removed by addition of sulfate salts which allow it to co-precipitate in the form of Ba(Ra)SO<sub>4</sub>. Therefore, co-precipitation of radium with barite (BaSO<sub>4</sub>), mostly via an inclusion (lattice replacement) process [7], is the main mechanism controlling radium behaviour in the waste streams and its migration in the environment [8,5]. To decontaminate uranium tailings or solid residues from, e.g. the petroleum industry, it is necessary to dissolve Ba(Ra)SO<sub>4</sub>.

Pure radium and barium sulfate salts and their co-precipitates are, in principle, insoluble in water and aqueous solutions of mineral acids and alkali at room temperature [9] (the recommended values for the logarithm of the BaSO<sub>4</sub> and RaSO<sub>4</sub> solubility products at zero ionic strength and 298 K are -9.95 and -10.21, respectively [10,11]). At room temperature, Ba(Ra)SO<sub>4</sub> can be dissolved using chelating agents. The most commercially available chelating agent for Ba(Ra)SO<sub>4</sub> dissolution is ethylenediaminetetraacetic acid (EDTA) and its derivatives. Aqueous alkaline EDTA solutions have been found to be effective in the dissolution of Ba(Ra)SO<sub>4</sub> and in the extraction of <sup>226</sup>Ra from uranium tailings [12]. Approximately 80-85 % of <sup>226</sup>Ra was extracted from uranium tailings using a 0.04 M aqueous alkaline EDTA solution at Elliot Lake, Ontario, Canada [13]. Moreover, alkaline EDTA solutions have been used for dissolution of irradiated <sup>226</sup>RaSO<sub>4</sub> targets and the preparation of <sup>227</sup>Ac/<sup>223</sup>Ra radiopharmaceutical generators [14]. One of the reasons for the high Ba(Ra)SO<sub>4</sub> solubility in alkaline EDTA solutions is the formation of a strong complex between Ba<sup>2+</sup> or Ra<sup>2+</sup> and EDTA. Therefore, it is necessary to know accurately the stability constants of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes to model the Ba(Ra)SO<sub>4</sub> dissolution equilibrium in alkaline EDTA systems including decontamination using EDTA.

Experimental studies of  $Ba^{2+}$  and  $Ra^{2+}$  complex formation are also important on a fundamental level. Radium and barium have similar solution chemistry and one of the main reasons for this is the similarity of the effective ionic radii, which are equal to 1.42 Å for  $Ba^{2+}$  and 1.48 Å for  $Ra^{2+}$  (in 8-fold coordination) [15]. Due to the high radiotoxicity of radium and its daughters, experimental thermodynamic data for radium are limited. For example, to the best of our knowledge, the experimental determination of radium activity coefficients or ion interaction parameters have never been reported in the literature. Due to the lack of experimental data, extrapolation of the ion interaction parameters for radium from values of the other alkaline-earth metals using ionic radii or using interaction parameters of barium directly are the methods used to calculate radium activity coefficients [5,16,17]. All approaches for modelling activity coefficient are semi-empirical, with one or more parameters either fitted or extrapolated, thus the obtained ion interaction parameters can be brought into question. Therefore, an experimental study of  $Ba^{2+}$  and  $Ra^{2+}$  complex formation using a background electrolyte would be beneficial on both applied and fundamental levels.

The objective of this work was to study the complex formation of  $Ra^{2+}$ , as well as  $Ba^{2+}$ , with EDTA as a function of ionic strength using NaCl as an ionic medium. Sodium chloride is an inert ionic electrolyte which is also omnipresent in the environment. Due to the high radiotoxicity of radium, the complex formation was studied via an ion exchange method which only requires trace amounts of radium. The specific ion interaction theory (SIT) was used to extrapolate the apparent stability constants of the studied complexes to zero ionic strength, and for determining the ion interaction parameters of the species involved in the complex formation.

#### 2. Experimental

#### 2.1 Sample preparation

The complexation of Ba<sup>2+</sup> and Ra<sup>2+</sup> with EDTA was studied as a function of NaCl ionic strength (0.22, 0.5, 1.0, 2.0 and 2.5 M) via an ion exchange method with batch and radiotracer techniques. The method is based on the different distribution of metal ions (133Ba2+ or 226Ra2+) and negatively charged metal-EDTA complexes using a strong cation exchange resin. Distribution experiments were performed in polypropylene tubes with aqueous phase volumes of 10 ml in the case of Ba<sup>2+</sup>, and 1 ml in the case of Ra<sup>2+</sup>, with 0.5 g and 0.05 g of ion exchange resin added to each tube, respectively. The ionic strength in the aqueous phase was adjusted using concentrated NaCl stock solutions. Different doses of Na<sub>2</sub>EDTA stock solution were added to each sample and its concentration was varied throughout the sample series, ranging between 0 and 6.67.10<sup>-5</sup> mol·1<sup>-1</sup>. The apparent EDTA dissociation constants at various NaCl ionic strengths were determined using the SIT methodology and the H<sup>+</sup> concentration was adjusted using potentiometric titrations to maximize the molar fractions of EDTA<sup>4-</sup> ( $-\log [H^+] = 12.4$ ; more than 99 % EDTA<sup>4-</sup>) or HEDTA<sup>3-</sup> (-log  $[H^+]=7.9-8.3$  depending on the ionic strength; always more than 98 % HEDTA<sup>3-</sup>). Samples without the ion exchange resin and EDTA were prepared to measure the total radioactivity of  ${}^{133}Ba^{2+}$  or <sup>226</sup>Ra<sup>2+</sup> in the sample. Preliminary kinetic studies confirmed that the metal-EDTA equilibria were achieved within 24 hours under the experimental conditions used. The experiments were performed in duplicate where each series contained 11 samples per ionic strength. All samples were kept at  $25 \pm 1$  °C.

#### 2.2 Reagents and chemicals

All aqueous solutions were prepared using MQ water with 18.2 M $\Omega$ ·cm resistivity at 25 °C and a total organic content of less than 5 mg·l<sup>-1</sup>. The barium stock solution was in the form of <sup>133</sup>Ba with a specific activity of 37 kBq·µl<sup>-1</sup> in 0.1 M HCl with an additional 10 µg·ml<sup>-1</sup> of BaCl<sub>2</sub> carrier (Eckert and Ziegler Isotope Products). Radium carbonate was synthesized from RaSO<sub>4</sub> powder as previously described [9]. The synthesized RaCO<sub>3</sub> was dissolved in 0.1 M HCl (Sigma-Aldrich 99.999% trace metals basis) to obtain 14 ml of radium stock solution with a <sup>226</sup>Ra specific activity of (2.5±0.1)·10<sup>4</sup> Bq·µl<sup>-1</sup>. The cation exchange resin was in sodium form (Biorad AG 50W-X8 200-400 mesh). EDTA stock solutions were prepared from solid Na<sub>2</sub>EDTA·2H<sub>2</sub>O (Sigma p.a. ≥99.0 %). The ionic strength and –log [H<sup>+</sup>] were adjusted using a NaCl stock solution prepared from solid NaCl (Sigma-Aldrich ACS reagent p.a. ≥99.0 %) and standard NaOH and HCl solutions (Fixanal, Sigma-Aldrich).

#### 2.3 Apparatus

All solid chemicals were weighed on a standard analytical balance (Sartorius Quintix125D-1S) and samples were kept at a constant temperature of  $25 \pm 1$  °C in a shaking water bath (Julabo SW23). Potentiometric measurements were performed using two pH meters coupled with combined glass electrodes (827 pH laboratory Metrohm coupled with Metrohm Primatrode electrode and Radiometer MeterLab PHM240 coupled with Radiometer PHC3006-9 electrode). Both electrodes were filled with a 3 M NaCl reference electrolyte and calibrated using the activity scale with standard buffer solutions (NIST and SRM traceable, Certipur, Merck), and were subsequently calibrated in the concentration scale using a potentiometric titration with negligible volume change [18]. The radioactivity of <sup>133</sup>Ba was measured using Liquid Scintillation Counting (LSC) (Perkin Elmer Guardian 1414) and aqueous <sup>133</sup>Ba samples were subsequently mixed with an Emulsifier safe LSC cocktail. The radioactivity of <sup>226</sup>Ra was measured using two High Purity Germanium Detectors (HPGe) (Canberra GEM23195 closed-end coaxial HPGe detector coupled with digital spectrum analyzer Canberra-2000/A and Ortec GEM-C5060 coaxial HPGe coupled with digital spectrum analyzer Canberra-2000/A and Ortec GEM-C5060 coaxial HPGe coupled with digital spectrum analyzer Canberra-2000/A and Ortec GEM-C5060 coaxial HPGe coupled with digital spectrum analyzer Ortec DSPEC50). Both detectors were calibrated using a mixed radionuclide reference solution (NIST traceable, Eckert and Ziegler). Nuclide half-lives, gamma emission energies and photon emission probabilities were taken from the Decay Data Evaluation Project [19].

#### 3. The model

The speciation of a metal ion  $(M^{2+})$  with various forms of EDTA can be described by the reaction:

$$M^{2+} + [H_r EDTA^{(r-4)}] \rightleftharpoons [MH_r EDTA^{(r-2)}]$$
(1)

where  $0 \le r \le 6$ .

The stability constant for reaction (1) at zero ionic strength is defined as:

$$K_{MH_{r}EDTA^{(r-2)}}^{o} = K_{MH_{r}EDTA^{(r-2)}} \cdot \frac{\gamma_{MH_{r}EDTA^{(r-2)}}}{\gamma_{M^{2+}} \cdot \gamma_{H_{r}EDTA^{(r-4)}}} = \frac{[MH_{r}EDTA^{(r-2)}]}{[M^{2+}] \cdot [H_{r}EDTA^{(r-4)}]} \cdot \frac{\gamma_{MH_{r}EDTA^{(r-2)}}}{\gamma_{M^{2+}} \cdot \gamma_{H_{r}EDTA^{(r-4)}}}$$
(2)

The SIT model developed by Brønsted [20,21], Scatchard [22], Guggenheim and Turgeon [23] can be used to express the activity coefficients  $\gamma_i$  of an ion *i* at ionic strengths below about 3.5 mol·kg<sup>-1</sup>:

$$\log_{10}\gamma_i = -z_i^2 \cdot D + \sum_i \varepsilon(i, j, I_m) \cdot m_i \tag{3}$$

where  $z_i$  is the charge of the ion  $i, \varepsilon(i,j)$  is the interaction parameter of ion i with all oppositely charged ions  $j, m_i$  is molal concentration of ion i and D is the Debye-Hückel term which is defined as:

$$D = \frac{A \cdot \sqrt{I_m}}{1 + 1.5 \cdot \sqrt{I_m}} \tag{4}$$

where *A* is a temperature dependent constant equal to 0.5090 and 0.5047 kg<sup>1/2</sup>·mol<sup>-1/2</sup> at 25 °C and 20 °C, respectively, for aqueous solutions [24],  $I_m$  is ionic strength in mol·kg<sup>-1</sup>. The value 1.5 is the product of *B* 

(a constant dependent on temperature and the solvent relative permittivity) and *a* (distance of closest approach or effective Debye-Hückel ionic radius). In the SIT, this product is usually taken to be 1.5 to minimize the effect of ionic strength on the ion interaction parameters. In this work, each ionic strength of NaCl was recalculated to the molal scale (from molar) using the relevant conversion factors [24]. Substituting the activity coefficients calculated using Eq.(3) into Eq.(2) yields:

$$\log_{10} K_{\rm MH_r EDTA^{(r-2)}} - \Delta z^2 \cdot D = \log_{10} K_{\rm MH_r EDTA^{(r-2)}}^{\rm o} - \Delta \varepsilon \cdot I_m$$
(5)

From Eq.5 it can be concluded that plotting the difference between the determined logarithm of the apparent stability constants and  $\Delta z^2 \cdot D$  against ionic strength of the same background electrolyte will result in an intercept which is the logarithm of the stability constant at zero ionic strength and a slope which is the ion interaction parameter term.

Measurement of the metal ion radioactivity in the aqueous phase allows for calculation of the distribution ratio between the solid phase and the aqueous phase according to:

$$D = \left(\frac{A_{total} - A_{aq}}{A_{aq}}\right) \cdot \frac{V}{m}$$
(6)

where  $A_{total}$  is the total radioactivity of the metal ion in the sample,  $A_{aq}$  is the radioactivity of the metal ion in the aqueous phase after the distribution equilibrium has been reached, V is the solution volume (ml) and m is the mass of the ion exchange resin (g).

The distribution ratio can also be expressed through the apparent stability constant:

$$D = \frac{\lambda \cdot [M^{2+}]}{[M^{2+}] + \sum (K_{MH_r EDTA}^{(r-2)} \cdot [M^{2+}] \cdot [H_r EDTA^{(r-4)}])}$$
(7)

where  $\lambda$  is the distribution ratio without the ligand (ml·g<sup>-1</sup>) and *K* is the apparent stability constant for the MH<sub>r</sub>EDTA<sup>(r-2)</sup> complex.

The apparent dissociation constants of the  $H_rEDTA^{(r-4)}$  complexes can be computed via the SIT (Eq. 3) using the EDTA dissociation constants at zero ionic strength and their ion interaction parameters given in the literature [25]. The constants calculated in this manner have been used in this work. Molar fractions of the different EDTA species can be computed as a function of hydrogen ion concentration using the calculated apparent dissociation constants of  $H_rEDTA^{(r-4)}$ . The concentration of  $H^+$  at which the molar fractions of EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> are maximized were calculated for all studied ionic strengths, and –log  $[H^+]$  was adjusted according to these calculations.

The hydrolysis of  $Ba^{2+}$  and  $Ra^{2+}$  at a  $-\log [H^+]$  of 12.4 (the highest  $-\log [H^+]$  used in this work) can be neglected [26] compared to the metals strong complexation with EDTA. Polynuclear complexes are also

not formed when a metal ion is at radiotracer levels, therefore the  $M^{2+}$  concentration terms in Eq. (7) can be cancelled. As a result, Eq. (7) can be simplified to:

$$K_{\mathrm{MH}_{r}\mathrm{EDTA}^{(r-2)}} \cdot [\mathrm{H}_{r}\mathrm{EDTA}^{(r-4)}] = \frac{\lambda}{D} - 1$$
(8)

Thus, according to Eq. (8) and under the experimental conditions studied, where only one form of  $H_r EDTA^{(r-4)}$  is dominant, the apparent stability constants of the  $MH_r EDTA^{(r-2)}$  complexes can be determined using linear regression.

The [H<sub>r</sub>EDTA<sup>(r-4)</sup>] term in Eq. (8) refers to the *free* concentration of the ligand. However, EDTA also forms strong complexes with Na<sup>+</sup>, which was used as part of the ionic medium. The Na<sup>+</sup> concentration was considerably higher than the  $M^{2+}$  concentration under all experimental conditions. As a result, the concentration of free EDTA was adjusted by the EDTA complex formation with Na<sup>+</sup>. The effect of complex formation between EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> with Na<sup>+</sup> has been found to be important [27] and can be described by the following reactions:

$$Na^{+} + EDTA^{4-} \rightleftharpoons NaEDTA^{3-}$$
(9)

$$Na^{+} + HEDTA^{3-} \rightleftharpoons NaHEDTA^{2-}$$
(10)

As a result, the *free* EDTA<sup>4-</sup> or HEDTA<sup>3-</sup> concentration in Eq. (8) can be expressed as:

$$[EDTA_{free}^{4-}] = \frac{[EDTA_{total}^{4-}]}{1 + K^{HEDTA} \cdot [H^+] + K^{NaEDTA} \cdot [Na^+]}$$
(11)

$$[\text{HEDTA}_{free}^{3-}] = \frac{[\text{EDTA}_{total}^{4-}]}{1 + \frac{[\text{H}^+]}{K^{\text{HEDTA}}} + K^{\text{NaHEDTA}} \cdot [\text{Na}^+]}$$
(12)

where  $K^{\text{HEDTA}}$  refers to the protonation constant of EDTA<sup>4-</sup> and  $K^{\text{NaEDTA}}$  or  $K^{\text{NaHEDTA}}$  refer to the stability constants for the reactions (9) and (10), respectively.

#### 4. **Results and discussion**

#### 4.1 Sodium speciation with EDTA

The dissociation constant of EDTA and stability constant for reaction (9) have been experimentally studied by many researchers and a comprehensive review is available [25]. The values of the protonation constants and the NaEDTA<sup>3-</sup> stability constant at zero ionic strength were taken from Hummel and co-workers [25] and are listed in Table 1. The SIT ion interaction parameters and associated uncertainties were derived from all available experimental data of NaEDTA<sup>3-</sup> and EDTA<sup>4-</sup> protonation in NaCl media at 25 °C listed in the review [25]. Subsequently, the apparent stability constants were calculated using the derived SIT ion interaction parameters. The apparent EDTA<sup>4-</sup> protonation constants and NaEDTA<sup>3-</sup> stability constants obtained were used to calculate the  $Ba^{2+}$  and  $Ra^{2+}$  stability constants (see Table 5) and free EDTA<sup>4-</sup> concentration (Eq. (11)), respectively. All these stability constants are listed in Table 1.

Equilibrium reaction	$I_m (\mathrm{mol}\cdot\mathrm{kg}^{-1})$	Stability constant $\log_{10} K$	Specific ion
			interaction parameters
			(NaCl) $\Delta \varepsilon$ (mol·kg <sup>-1</sup> )
$H^+ + HEDTA^{3-} \rightleftharpoons H_2EDTA^{2-}$	0	$6.80\pm0.02$	$0.40\pm0.03$
H <sup>+</sup> + EDTA <sup>4-</sup> ≓ HEDTA <sup>3-</sup>	0	$11.24\pm0.03$	$0.55 \pm 0.04$
	0.22	$10.24\pm0.03$	
	0.51	$10.12\pm0.03$	
	1.02	$10.21\pm0.04$	
	2.09	$10.51\pm0.06$	
	2.64	$10.74\pm0.08$	]
Na⁺ + EDTA⁴- ≓ NaEDTA³-	0	$2.80\pm0.20$	$0.27 \pm 0.33$
	0.22	$1.74\pm0.22$	
	0.51	$1.54\pm0.31$	
	1.02	$1.44 \pm 0.52$	
	2.09	$1.51 \pm 1.0$	
	2.64	$1.59 \pm 1.3$	]

Table 1. Stability constants and SIT ion interaction parameters at 25 °C used in this work

Only a few experimental data for the formation of the NaHEDTA<sup>2-</sup> complex (Eq. (10)) are available in the literature and the reported log<sub>10</sub> K° values vary significantly from 0 to 1.5 [28-31]. The main reason for the  $\log_{10} K^{\circ}$  data discrepancies is that the NaHEDTA<sup>2-</sup> complex is quite weak. In the case of weak complex formation it is usually impossible to separate the weak complex formation effect from potential activity coefficient changes. This and other challenges associated with the determination of the stability constants of weak complexes have been previously discussed in detail [32,33]. Perhaps, the most reasonable value for the stability constant of the NaHEDTA<sup>2-</sup> complex was reported by Palaty [30]. The author used ion selective electrodes to study the proton dissociation reactions of EDTA and the sodium-EDTA equilibrium and the obtained stability constant values are in good agreement with the values listed in Table 1 (11.34, 6.81 and 2.61, respectively [30]). Tetramethylammonium chloride was used as the background electrolyte with a total ionic strength of  $0.12 \text{ mol} \cdot 1^{-1}$ . The temperature was not given by the author [30] but based on all the obtained values it can be assumed that the reported equilibria were studied at 25 °C. The reported value for the  $log_{10} K^{\circ}$  value of the NaHEDTA<sup>2-</sup> complex was -0.03. The value is subject to some uncertainty and it is assumed that the actual  $\log_{10} K^{\circ}$  value at zero ionic strength lies in the range from -0.5 to 0.5 (i.e.  $\log_{10} K = 0 \pm 0.5$ ). Most probably, the assignment of such a high, but reasonable, uncertainty for the stability constant of a weak complex is the only way to overcome the lack of reliable data. The proposed  $\log_{10} K^{\circ}$ value of  $0 \pm 0.5$  is in accord with the statement made by Marcus and Hefter in relation to  $\log_{10} K^{\circ}$  values less than 1, where substantial care needs to be taken in obtaining the exact magnitude of such constants by either experiment or theory [33].

To be able to extrapolate the  $\log_{10} K^{\circ}$  value of  $0 \pm 0.5$  for the NaHEDTA<sup>2-</sup> complex at the ionic strengths used in this work, it is necessary to know the following SIT interaction parameters:  $\varepsilon(Na^+, Cl^-)$ ,  $\varepsilon(Na^+, HEDTA^{3-})$  and  $\varepsilon(Na^+, NaHEDTA^{2-})$ . The first two parameters, with their associated uncertainties, are available in the literature [24,25] and to the best of our knowledge the last parameter has never been

reported. A comparison of the sodium SIT ion interactions with many different negatively charged ligands shows that this parameter usually varies from -0.3 to 0.1 [24] (the sodium ion with a divalent anion). Moreover, the sodium SIT ion interaction with ligands similar to H<sub>2</sub>EDTA<sup>2-</sup> is -0.37 [25]. Consequently, based on these values, the  $\varepsilon(Na^+, NaHEDTA^{2-})$  SIT parameter has been estimated as -(0.2 ± 0.3) kg·mol<sup>-1</sup>. All the parameters associated with the NaHEDTA<sup>2-</sup> complex (Eq. (10)) used in this work are listed in Table 2.

Parameter	Value	Reference	
$\log_{10} K^{\circ}$	0 + 0.5	Estimated in this work, based on available	
	$0 \pm 0.3$	experimental data from Palaty [30]	
$\epsilon(Na^+, Cl^-)$	$0.03 \pm 0.01 \text{ (kg} \cdot \text{mol}^{-1}\text{)}$	Guillaumont et al. [24]	
ε(Na <sup>+</sup> , HEDTA <sup>3-</sup> )	$-(0.1 \pm 0.14) (\text{kg} \cdot \text{mol}^{-1})$	Hummel et al. [25]	
ε(Na <sup>+</sup> , NaHEDTA <sup>2-</sup> )	$-(0.2 \pm 0.3) (\text{kg} \cdot \text{mol}^{-1})$	Estimated in this work	

Table 2. Stability constants and SIT ion interaction parameters for the NaHEDTA<sup>2-</sup> complex formation (Eq. 2) at 25 °C

#### 4.2 Stability constants for the complex formation of Ba<sup>2+</sup> and Ra<sup>2+</sup> with EDTA

The apparent stability constants for the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes were obtained from distribution coefficients (from the experiments conducted at a –log [H<sup>+</sup>] of 12.4) using a weighted linear regression ( $\omega_i = \sigma_i$ ) with a zero intercept (Eq. (8)). The free EDTA<sup>4-</sup> concentrations were obtained by correcting for the formation of the NaEDTA<sup>3-</sup> complex (Eq. (9)) using Eq. (11) and the values which are listed in Table 1. The standard deviations of the free EDTA<sup>4-</sup> concentrations were propagated from the standard deviation of the apparent NaEDTA<sup>3-</sup> stability constants, also listed in Table 1. The standard deviation ratio without the ligand ( $\lambda$ ) and the distribution ratio with the ligand (D) were calculated based on duplicate series (biased standard deviation with (n-1) in the denominator) and were propagated to the standard deviations of ( $\lambda$ /D - 1). Standard uncertainty propagation was used in the both cases.

The uncertainty in the linear fitting were obtained using the method of Allard and Ekberg [34]. After obtaining the uncertainties in both the ( $\lambda$ /D - 1) term and the free EDTA concentration, 30 points were sampled from each uncertainty space using a normal distribution with the mean and standard deviation obtained. Thus, the obtained simulated data points covered the entire standard deviation region in both x and y forming confidence ellipses for each point. Negative simulated values of the free EDTA<sup>4-</sup> concentrations were discarded. All these points were then used for the linear regression and the estimation of the associated uncertainty analysis.

The weighted mean and associated 95 % confidence intervals of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> stability constants at zero ionic strength were calculated from the values listed in Tables 3 and 4.

Figure 1 shows a representative dataset for the linear regression of the BaEDTA<sup>2-</sup> (reaction 1) apparent stability constant in 0.22 mol·kg<sup>-1</sup> NaCl.



**Fig. 1** Determination of BaEDTA<sup>2-</sup> apparent stability constants using linear regression ( $0.22 \text{ mol}\cdot\text{kg}^{-1}\text{NaCl}$ , reaction 1, Eq. 8)

As can be observed from Fig. 1, the standard deviations of the free EDTA<sup>4-</sup> concentrations are large and increase with an increase in ionic strength (NaCl). These large standard deviations are a consequence of the error propagation, that result principally from the large uncertainties in the NaEDTA<sup>3-</sup> stability constants (Table 1).

The stability constants obtained are listed in Table 3 and extrapolation of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> stability constants to zero ionic strength (non-weighted linear regression) using the SIT are shown in Fig. 2.

$I_m$ (mol·kg <sup>-1</sup> )	$\log_{10} K_{ m BaEDTA}$	$\log_{10} K_{ m RaEDTA}$
0	$9.88 \pm 0.11$	$9.11\pm0.09$
0.22	$7.70\pm0.08$	$6.96\pm0.20^*$
0.51	$7.38\pm0.08$	$6.60\pm0.08$
1.02	$6.99\pm0.12$	$6.42\pm0.10$
2.09	$7.10\pm0.08$	$6.60\pm0.10$
2.64	$7.16\pm0.08$	$6.63\pm0.08$

Table 3. Apparent stability constants of BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> aqueous complexes in NaCl media at 25°C formed via reaction (1)

Ionic strengths were adjusted from the mol·l<sup>-1</sup> to mol·kg<sup>-1</sup> scale using the appropriate conversion factors [24]. Uncertainties correspond to 95 % confidence intervals. \* estimated uncertainty.



**Fig. 2** Extrapolation of BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> apparent stability constants (NaCl media, reaction 1) to zero ionic strength using SIT

As can be observed from Fig. 2, the fits are satisfactory and the experimental data are accurately modelled by the SIT. According to the calculations, the effect of Na<sup>+</sup> complex formation with EDTA<sup>4-</sup> (Eq. (9)) is significant and the difference between the corrected and uncorrected stability constants of both BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> at zero ionic strength is more than 1 log unit. The difference between the slopes (with and without correction for Na complex formation with EDTA), which corresponds to the ion interaction parameter term, was also significant and the deviation of the experimental data points from the regression line was higher at increased ionic strength. This strongly indicates that the complex formation between sodium and EDTA is significant, which is in agreement with previous studies [27].

The apparent stability constants, assuming only the formation of the BaHEDTA<sup>-</sup> and RaHEDTA<sup>-</sup> complexes (according to reaction (1) (r = 1)), were derived from the experiments conducted at a  $-\log [H^+]$  of 7.9 - 8.3 with the mole fraction of HEDTA<sup>3-</sup> being more than 98 % using the same method as used for derivation of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complex stability constants. The apparent stability constants obtained were extrapolated to zero ionic strength using the SIT that resulted in stability constants of  $\log_{10} K^\circ = 7.34 \pm 0.30$  (for BaHEDTA<sup>-</sup>) and  $\log_{10} K^\circ = 6.57 \pm 0.30$  (for RaHEDTA<sup>-</sup>). Schwarzenbach and Ackermann [35] have previously given a  $\log_{10} K$  value for the same reaction (BaHEDTA<sup>-</sup> complex) of 2.07

at 20 °C and an ionic strength of 0.1 M. This value, when extrapolated to zero ionic strength, results in  $\log_{10} K^{\circ} = 3.15$ , which is much lower than the value obtained in the present work. It can be seen that the value from this study is more than four orders of magnitude larger than the value given by Schwarzenbach and Ackermann. There are two probable reasons for the disagreement between these two values: either the assumption that the BaHEDTA<sup>-</sup> complex is formed according to reaction (1) (r = 1) at  $-\log [H^+]$  of 7.9 - 8.3 is not valid or the data from Schwarzenbach and Ackermann are inconsistent. The latest hypothesis can be verified by combining the data from Schwarzenbach and Ackermann [35] with other literature data [36,37], where the stability constants for the reaction of various metals with EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> are reported for the same experimental conditions (20 °C and an ionic strength of 0.1 M) and performing a linear free energy analysis of the data. This analysis (i.e. a plot of the log *K* values of M<sup>n+</sup> - EDTA<sup>4-</sup> complexes against the log *K* of M<sup>n+</sup> - HEDTA<sup>3-</sup> complexes, where M<sup>n+</sup> is a metal ion with n  $\geq 2$  (reaction (1) with r = 0 and r = 1, respectively)) is shown in Fig. 3.



**Fig. 3** Linear free energy analysis of available literature data [36,37,35] for the logarithm of  $M^{n+}EDTA^{(4-n)}$  and  $M^{n+}HEDTA^{(3-n)}$  apparent stability constants ( $n \ge 2$ ) at the same experimental conditions (20 °C, I = 0.1 M)

As shown in Fig. 3 there is a strong relationship between the magnitude ( $\log_{10} K$  values) of the M<sup>n+</sup>EDTA<sup>(4-n)</sup> and M<sup>n+</sup>HEDTA<sup>(3-n)</sup> stability constants ( $n \ge 2$ ), and consequently, the available literature data [36,37,35] are consistent. Therefore, the assumption that only the BaHEDTA<sup>-</sup> or RaHEDTA<sup>-</sup> complexes are formed at a –log [H<sup>+</sup>] of 7.9 - 8.3 is not valid. The stability constant for the BaHEDTA<sup>-</sup> complex derived in the present study is more than four orders of magnitude larger when compared to those values available in the literature
which indicates that another stronger complex dominates at a -log  $[H^+]$  of 7.9 - 8.3. The only other strong complex which could be formed in the studied system is BaEDTA<sup>2-</sup> (or RaEDTA<sup>2-</sup>). The likely mechanism of the formation of these two complexes at a -log  $[H^+]$  of 7.9 - 8.3, where the mole fraction of HEDTA<sup>3-</sup> is more than 98 % is as follows:

$$Ba^{2+} + HEDTA^{3-} \rightleftharpoons BaEDTA^{2-} + H^{+}$$
(13)

$$Ra^{2+} + HEDTA^{3-} \rightleftharpoons RaEDTA^{2-} + H^{+}$$
<sup>(14)</sup>

If the proposed reactions (13-14) occur in the studied system, then Eq. (7) can be adopted to reactions (13-14) to describe the experimental data obtained at  $a -\log[H^+]$  of 7.9 - 8.3:

$$K_{M_{r} \in DTA^{(r-4)}} \cdot \frac{[\text{HEDTA}^{3-}]}{[\text{H}^{+}]} = \frac{\lambda}{D} - 1$$
(15)

According to Eq. (15), the concentration of the free HEDTA<sup>3-</sup> must be divided by the H<sup>+</sup> concentration to obtain the apparent stability constant for the BaEDTA<sup>2-</sup> or RaEDTA<sup>2-</sup> complex via reactions (13-14) under these lower –log [H<sup>+</sup>] conditions. Moreover, it can be shown that the sum of the logarithm of obtained stability constants for reactions (13-14) and the logarithm of the protonation constant of EDTA<sup>4-</sup> results in the stability constant for the BaEDTA<sup>2-</sup> or RaEDTA<sup>2-</sup> complexes formed via reaction (1) with r = 0. The stability constants for reactions (13-14) occurred at a –log [H<sup>+</sup>] of 7.9 - 8.3 and associated standard deviations were derived using the same method as was used to derive stability constants and standard deviations for reaction (1) with r = 0 at a –log [H<sup>+</sup>] of 12.4. These stability constants and the calculated stability constants for reaction (1) with r = 0, using the derived constants and the protonation constants of EDTA<sup>4-</sup> from Table 1, are listed in Table 4. Extrapolation of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> stability constants to zero ionic strength using the SIT is shown in Fig. 4.

Table 4. Apparent stability constants of BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> aqueous complexes in NaCl media at 25°C formed via reactions (13-14) and (1)

$I_m$ (mol·kg <sup>-1</sup> )	$\begin{array}{c} \log_{10} K_{\text{BaEDTA}} \\ \text{(formed via} \\ \text{reaction 13)} \end{array}$	$log_{10} K_{BaEDTA}$ (formed via reaction 1)	$log_{10} K_{RaEDTA}$ (formed via reaction 14)	$\log_{10} K_{RaEDTA}$ (formed via reaction 1)
0	$-1.41 \pm 0.12$	$9.83\pm0.14$	$-2.07 \pm 0.11$	$9.17\pm0.13$
0.22	$-2.63\pm0.06$	$7.61\pm0.08$	$-3.26\pm0.06$	$6.98\pm0.08$
0.51	$-2.80\pm0.08$	$7.32\pm0.10$	$-3.42\pm0.08$	$6.71\pm0.10$
1.02	$-3.21\pm0.08$	$7.00\pm0.11$	$-3.85\pm0.08$	$6.37\pm0.11$
2.09	$-3.49\pm0.08$	$7.02\pm0.14$	$-4.15 \pm 0.10$	$6.36\pm0.15$
2.64	$-3.75 \pm 0.08$	$6.99 \pm 0.18$	$-4.24 \pm 0.08$	$6.50 \pm 0.18$

Ionic strengths were adjusted from the mol·l<sup>-1</sup> to mol·kg<sup>-1</sup> scale using the appropriate conversion factors [24] and  $\log_{10} K_{\text{BaEDTA}}$  or  $\log_{10} K_{\text{RaEDTA}}$  for the reaction 13-14 were calculated using EDTA<sup>4-</sup> protonation constants listed in Table 1. Uncertainties correspond to 95 % confidence interval



**Fig. 4** Extrapolation of BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> apparent stability constants (NaCl media, reaction 13-14) to zero ionic strength using the SIT

As can be observed in Fig. 4, the experimental data are accurately described by Eq. (15). A comparison of the stability constants of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes formed via reaction (1) listed in Table 4 with the same stability constants listed in Table 3 shows that all the values are within the 95 % confidence interval. This strongly indicates that the proposed reactions (13-14) occur at the pH region where the HEDTA<sup>3-</sup> species dominates. The effect of Na<sup>+</sup> complex formation with HEDTA<sup>3-</sup> (Eq. (10)) was not as significant as in the case of EDTA<sup>4-</sup> due to the fact that the NaHEDTA<sup>2-</sup> complex is much weaker than NaEDTA<sup>3-</sup> (Tables 1 and 2).

A comparison of the average value of the obtained metal-EDTA stability constants at zero ionic strength with data available in the literature is shown in Table 5. The data from the literature were, where necessary, extrapolated to zero ionic strength using the Davies equation [38] (in the last term  $0.2 \cdot I$  was used instead of  $0.3 \cdot I$ , the latter as proposed by Davies [39]) for activity coefficient corrections. The weighted mean and associated 95 % confidence intervals of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> stability constants at zero ionic strength were calculated from the values listed in Tables 3 and 4.

Method	Ionic medium	Temperature (°C)	Reported log <sub>10</sub> K	Extrapolated to zero ionic strength $\log_{10}$ $K^{\circ}$	Reference		
$Ba^{2+} + EDTA^{4-} \rightleftharpoons BaEDTA^{2-}$							
Ion exchange	0.2; 0.5; 1; 2; 2.5 M (NaCl)	25	Tables 3 and 4	$9.86\pm0.09$	This work		
Review	0.1 M	25	$\begin{array}{c} 7.86 \pm \\ 0.08 \end{array}$	9.64	Smith and Martell [36]		
рН	0.1 M (KCl)	20	7.76	9.54	Schwarzenbach and Ackermann [35]		
рН	0.1 M <sup>a</sup>	25	7.73	9.51	Carini and Martell [40]		
рН	0.1 M	25	7.9	9.68	Schmid and Reilley [41]		
Ion exchange	0	25	9.92	9.92	Astakhov and Fomenko [42]		
pH	0.1 M (KNO <sub>3</sub> )	25	7.63	9.41	Bohigian and Martell [43]		
Paper electrophoresis	0.1 M (KNO <sub>3</sub> )	20	8	9.78	Jokl and Majer [44]		
рН	0.1 M (KNO <sub>3</sub> or (CH <sub>3</sub> ) <sub>4</sub> N(NO <sub>3</sub> ) )	25	7.8	9.58	Delgado and Da Silva [45]		
$Ra^{2+} + EDTA^{4-} \rightleftharpoons RaEDTA^{2-}$							
Ion exchange	0.2; 0.5; 1; 2; 2.5 M (NaCl)	25	Table 3	$9.13\pm0.07$	This work		
Ion exchange	0.1 M <sup>a</sup>	20ª	7.12	8.9	Nikolsky et al [46]		
Ion exchange	0.1 M (sodium salt) <sup>b</sup>	20	$\begin{array}{c} 7.07 \pm \\ 0.06^{\mathrm{b}} \end{array}$	9.22 <sup>b</sup>	Baetsle and Bengsch [47]		
Solvent extraction	0.1 M (NaClO <sub>4</sub> )	25	7.7	9.29	Sekine et al [48]		
Estimated	0.1 M	25	7.4	9.2	Nelson et al [49]		

Table 5. Comparison of reported stability constants for the formation of BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup>

<sup>a</sup> ionic strength and temperature were assumed, <sup>b</sup> contribution of the 0.01 mol·1<sup>-1</sup> EDTA to the total ionic strength has been considered Experimental data for the stability constant of BaEDTA<sup>2-</sup> [42,43,40,45,44,41,35] and reviews of relevant stability constants [50,36] are available in the literature. The data given in Table 5 for extrapolation of the literature data for the stability constant of BaEDTA<sup>2-</sup> to zero ionic strength are in very good agreement with the value determined in the present work.

The complex formation of radium with EDTA has been studied by several researchers using the ion exchange or solvent extraction methods and the experimental data have been reviewed [50,51]. Nikolsky and co-workers were the first to study RaEDTA<sup>2-</sup> complex formation and obtained a  $\log_{10} K$  value of 7.12 for RaEDTA<sup>2-</sup> [46]. The value was extrapolated to zero ionic strength assuming a temperature of 20 °C and an ionic strength of 0.1 mol·l<sup>-1</sup>. Baetsle and Bengsch studied RaEDTA<sup>2-</sup> complex formation using an ion exchange resin (Amberlite IR120) at 20 °C and an ionic strength of 0.1 mol·1<sup>-1</sup> (sodium salt) and reported a  $\log_{10} K$  value of 7.07  $\pm$  0.06 [47]. The concentration of EDTA<sup>4-</sup> was 0.01 mol·1<sup>-1</sup> and an acetate buffer was used. Such a high concentration of EDTA<sup>4-</sup> has a significant influence on the ionic strength, and therefore, the actual ionic strength used was  $0.19 \text{ mol} \cdot l^{-1}$  and this value has been used to extrapolate the reported value to zero ionic strength. Sekine and co-workers used solvent extraction (a mixture of 0.1 M thenoyltrifluoroacetone and 0.1 M tributylphosphate in CCl<sub>4</sub>) to study Ra<sup>2+</sup> complex formation with various amino carboxylic acids at 25 °C and 0.1 mol·l<sup>-1</sup> NaClO<sub>4</sub> and obtained a  $log_{10}$  K value of 7.7 for the RaEDTA<sup>2-</sup> complex [48]. A  $\log_{10} K$  value for RaEDTA<sup>2-</sup> was also estimated to be 7.4 for 25 °C and an ionic strength of 0.1 mol·1<sup>-1</sup> by Nelson and co-workers [49]. The RaEDTA<sup>2-</sup> stability constant obtained in this work is in very good agreement with those of the other studies when taking into account differences in temperature, ionic strength and difficulties in analyzing the literature data (experimental details missing, high EDTA concentrations affecting the ionic media etc). Probably the best comparison of the RaEDTA<sup>2-</sup> stability constants obtained in this work is with work of Sekine and co-workers and values obtained for zero ionic strength from the two studies are in very good agreement.

The difference between  $\log_{10} K^{\circ}_{BaEDTA}^{2-}$  and  $\log_{10} K^{\circ}_{RaEDTA}^{2-}$  is 0.73 log units. The difference is relatively small which may indicate that the speciation of  $Ba^{2+}$ ,  $Ra^{2+}$ , and potentially other alkaline earth metals with EDTA<sup>4-</sup>, depends on the ionic radius of the metal ion. Extrapolation of the thermodynamic properties of radium, including stability constants, from the property values of other alkaline-earth metals using an electrostatic model is a widely used method [8]. A plot of the logarithm of stability constants of calcium (taken from [25]), strontium (taken from [36] and extrapolated to zero ionic strength using the Davies equation), barium and radium with EDTA<sup>4-</sup> at zero ionic strength and 25 °C against the effective ionic radii of these elements in 8-fold coordination (taken from Shannon [15]) is shown in Fig. 5.



**Fig. 5** Comparison of alkaline-earth metals – EDTA<sup>4-</sup> stability constants at zero ionic strength using their effective ionic radii in 8-fold coordination (ionic radii taken from Shannon [15])

As shown in Fig. 4, the fit is good for all alkaline-earth metals which likely indicates that the bonding between these alkaline-earth metals and EDTA<sup>4-</sup> is similar and relativistic or other effects do not occur. It also confirms that the electrostatic model is a useful tool for extrapolation of radium thermodynamic properties and obtaining a first estimate of stability constants for radium complexation.

## 4.3 SIT ion interaction parameters of Ba<sup>2+</sup> and Ra<sup>2+</sup>

According to the SIT model (Eq. (5)), the slopes are equal to the ion interaction parameters between oppositely charged ions. The slopes for the extrapolation to zero ionic strength in Fig. 1 and Fig. 3 yield the SIT ion interaction parameter terms shown in Eqs. (16)-(17) and (18)-(19), respectively:

$$\Delta \varepsilon_1^{\text{BaEDTA}} = \varepsilon(\text{Na}^+, \text{BaEDTA}^{2-}) - \varepsilon(\text{Ba}^{2+}, \text{Cl}^-) - \varepsilon(\text{Na}^+, \text{EDTA}^{4-})$$
(16)

$$\Delta \varepsilon_{1}^{\text{RaEDTA}} = \varepsilon(\text{Na}^{+}, \text{RaEDTA}^{2-}) - \varepsilon(\text{Ra}^{2+}, \text{Cl}^{-}) - \varepsilon(\text{Na}^{+}, \text{EDTA}^{4-})$$
(17)

$$\Delta \varepsilon_2^{\text{BaEDTA}} = \varepsilon(\text{Na}^+, \text{BaEDTA}^{2-}) + \varepsilon(\text{H}^+, \text{Cl}^-) - \varepsilon(\text{Ba}^{2+}, \text{Cl}^-) - \varepsilon(\text{Na}^+, \text{HEDTA}^{3-})$$
(18)

$$\Delta \varepsilon_2^{\text{RaEDTA}} = \varepsilon(\text{Na}^+, \text{RaEDTA}^{2^-}) + \varepsilon(\text{H}^+, \text{Cl}^-) - \varepsilon(\text{Ra}^{2^+}, \text{Cl}^-) - \varepsilon(\text{Na}^+, \text{HEDTA}^{3^-})$$
(19)

The SIT ion interaction parameters determined for Eqs. (16)-(19) and some other ion interactions relevant to the studied systems are listed in Table 6.

Interaction	SIT parameters (kg·mol <sup>-1</sup> )	Reference	
$\Delta \epsilon_1 (MgEDTA^{2-})$	-(0.52±0.04)	[25]	
$\Delta \epsilon_1 (CaEDTA^{2-})$	-(0.5±0.5)	[25]	
$\Delta \epsilon_1(BaEDTA^{2-})$	-(0.44±0.07)	Eq. 16 (This work)	
$\Delta \epsilon_1 (RaEDTA^{2-})$	-(0.54±0.06)	Eq. 17 (This work)	
$\Delta \epsilon_2(BaEDTA^{2-})$	$0.14{\pm}0.08$	Eq. 18 (This work)	
$\Delta \epsilon_2 (RaEDTA^{2-})$	0.10±0.07	Eq. 19 (This work)	
ε(Na <sup>+</sup> , EDTA <sup>4-</sup> )	0.32±0.14	[24]	
ε(Na <sup>+</sup> , HEDTA <sup>3-</sup> )	-(0.10±0.14)	[24]	
ε(H <sup>+</sup> , Cl <sup>-</sup> )	0.12±0.01	[24]	
ε(Ba <sup>2+</sup> , Cl <sup>-</sup> )	0.07±0.01	[24]	
ε(Na <sup>+</sup> , MgEDTA <sup>2-</sup> )	-(0.01±0.15)	[24]	
ε(Na <sup>+</sup> , BaEDTA <sup>2-</sup> )	-(0.03±0.11)	This work	
ε(Na <sup>+</sup> , RaEDTA <sup>2-</sup> )	-(0.10±0.11)*	This work	

Table 6. SIT ion interaction parameters kg·mol<sup>-1</sup> of some metal ions and ligands relevant to the studied systems at 25°C

Uncertainties correspond to 95 % confidence interval.

\* This value has been calculated using  $\varepsilon(Ba^{2+}, Cl^{-})$  as a substitute for  $\varepsilon(Ra^{2+}, Cl^{-})$ .

As shown in Table 6, the SIT parameters for all of the listed alkaline-earth metal ions are very similar. According to the SIT, interactions occur only between ions of opposite charge, which means that the alkaline-earth metal ions undergo similar short- and long-range electrostatic interactions with EDTA<sup>4-</sup> and Cl<sup>-</sup>. The SIT ion interaction parameters between Na<sup>+</sup> and BaEDTA<sup>2-</sup> can be calculated as a weighted mean (Eqs.(16) and (18)) and using the derived  $\Delta \varepsilon_1$ (BaEDTA<sup>2-</sup>) or  $\Delta \varepsilon_2$ (BaEDTA<sup>2-</sup>) and previously established ion interaction parameters:  $\varepsilon$ (Ba<sup>2+</sup>, Cl<sup>-</sup>),  $\varepsilon$ (H<sup>+</sup>, Cl<sup>-</sup>),  $\varepsilon$ (Na<sup>+</sup>, EDTA<sup>4-</sup>) and  $\varepsilon$ (Na<sup>+</sup>, HEDTA<sup>3-</sup>) [24]. The SIT ion interaction parameters between Na<sup>+</sup> and RaEDTA<sup>2-</sup> can be calculated using the same method, with  $\varepsilon$ (Ba<sup>2+</sup>, Cl<sup>-</sup>) continuing to substitute for  $\varepsilon$ (Ra<sup>2+</sup>, Cl<sup>-</sup>)). All parameters are listed in Table 6 and a comparison of the computed  $\varepsilon$ (Na<sup>+</sup>, BaEDTA<sup>2-</sup>) and  $\varepsilon$ (Na<sup>+</sup>, RaEDTA<sup>2-</sup>) parameters with  $\varepsilon$ (Na<sup>+</sup>, MgEDTA<sup>2-</sup>), taken from the literature [24], shows that all parameters are within the 95 % confidence intervals.

The barium ion interaction parameters are often used as a substitute for the radium parameters due to a lack of experimental data in the case of radium [5,16,17]. It is possible to verify this methodology by calculation of  $\Delta \epsilon_1$ (RaEDTA<sup>2-</sup>) or  $\Delta \epsilon_2$ (RaEDTA<sup>2-</sup>) (Eqs. (17) and (19)) using  $\epsilon$ (Na<sup>+</sup>, EDTA<sup>4-</sup>),  $\epsilon$ (Na<sup>+</sup>, HEDTA<sup>3-</sup>) and the barium SIT parameters listed in Table 6 as substitutes for unknown radium parameters (i.e.  $\epsilon$ (Na<sup>+</sup>, BaEDTA<sup>2-</sup>) instead of  $\epsilon$ (Na<sup>+</sup>, RaEDTA<sup>2-</sup>) and  $\epsilon$ (Ba<sup>2+</sup>, Cl<sup>-</sup>) instead of  $\epsilon$ (Ra<sup>2+</sup>, Cl<sup>-</sup>)). This results in  $\Delta \epsilon_1$ (RaEDTA<sup>2-</sup>) = -(0.42 \pm 0.18) and  $\Delta \epsilon_2$ (RaEDTA<sup>2-</sup>) = -(0.08 \pm 0.18) which are within the 95 % confidence intervals of the experimentally determined  $\Delta \epsilon_1$ (RaEDTA<sup>2-</sup>) and  $\Delta \epsilon_2$ (RaEDTA<sup>2-</sup>) and  $\epsilon_2$ (RaEDTA<sup>2-</sup>) and

## 5. Conclusion

The apparent stability constants of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes were determined over a wide range of NaCl concentrations (0.2-2.5 M) at 25 °C and in two pH regions where the EDTA<sup>4-</sup> and HEDTA<sup>3-</sup>

species dominate. The obtained constants were extrapolated to zero ionic strength using the SIT and compared with available literature data. It was found that in the pH region where the HEDTA<sup>3-</sup> species dominates, the reaction of  $Ba^{2+}$  or  $Ra^{2+}$  with the HEDTA<sup>3-</sup> ligand results in the formation of the BaEDTA<sup>2-</sup> and RaEDTA<sup>2-</sup> complexes and a proton and that formation of BaHEDTA<sup>-</sup> or RaHEDTA<sup>-</sup> does not occur in alkaline media. The similarity of the barium and radium ion interaction parameters indicates that both metal ions undergo almost identical short- and long-range electrostatic interactions with EDTA<sup>4-</sup> and Cl<sup>-</sup>. The results also show that using the SIT interaction parameters of  $Ba^{2+}$  as a substitute for missing  $Ra^{2+}$  SIT interaction parameters is a useful tool for the  $Ra^{2+} - NaCl - EDTA^{4-}$  system.

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