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On the solubility of radium sulfate and carbonate

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Radium sulfate powder

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Abstract

Radium is one of the most toxic elements and its concentration in different human activities and migration from man-made wastes provokes a strong interest in environmental science. To be able to model the migration process, reliable experimental thermodynamic data of radium compounds are needed.

In this work details of the safe radium source disassembly which were previously used in brachytherapy are described and different methods for conversion of $RaSO_4$ into aqueous solution are reviewed. The method of choice included three cycles of $RaSO_4$ heating in 1.5 M Na_2CO_3 up to 85 ºC, cooling and subsequent removal of supernatant. X-ray diffraction studies showed that the method allows the synthesis of amorphous $RaCO_3$, which can be dissolved in mineral acid. Gamma spectrometric measurements showed that most of the initial $RaSO_4$ was converted into solution and that 7 ± 1 % of the initial ^{210}Pb was co-precipitated with $RaCO_3$. Synthesized $RaCO_3$ was dissolved in HCl to prepare a radium stock solution.

The radium stock solution was used to determine the solubility of pure $RaSO_4$ and $RaCO_3$ from oversaturation using Na_2SO_4 and Na_2CO_3 as a source of sulfate and carbonate ions. The solubility was determined at 25.1 ºC as a function of ionic strength using NaCl media. The concentration of radium was measured by gamma spectrometry after separation of the aqueous phase from the solid phase using ultracentrifugation. The extended specific ion interaction theory was used to extrapolate solubility product constants to zero ionic strength ($\log_{10} K_{sp}° = -10.16 \pm 0.05$ for $RaSO_4$ and $\log_{10} K_{sp}° = -7.73 \pm 0.56$ for $RaCO_3$) and to calculate ion interaction coefficients.

A comparison of the shapes of the radium solubility curves for both anions with the shapes of corresponding barium solubility curves demonstrates the similarity of the behaviour of radium and barium salts in saline solutions. It can be supposed that due to the similarity of the radium and barium effective ionic radii, and the same charge, these ions undergo similar specific ion interactions in NaCl media.

Keywords: *radium sulfate, radium carbonate, solubility product, precipitation, dissolution, thermodynamics*

Contents

1. Introduction

Radium was discovered in 1898 by Pierre and Marie Curie, together with Gustave Bemont [CUR98]. The investigative discovery was based on an observation that the radioactivity of the natural uranium mineral, pitchblende (uraninite), was higher than that of uranium salts. Understanding that radioactivity is an atomic property, allowed the supposition that pitchblende consists of atoms of different radioactive elements. To validate this assumption, pitchblende was dissolved and radium was co-precipitated with its chemical analogue – barium and identified by measurement of its radioactivity. Later, in 1902, 90 mg of radium chloride was separated from 1 tonne of uranium ore tailings by co-precipitation and the atomic weight of radium was determined to be 225 [CUR04]. Metallic radium was obtained by Marie Curie and Andre Debierne using electrolysis of radium chloride on a mercury cathode and subsequent distillation in a hydrogen atmosphere [CUR10]. These experiments proved that radium is the heaviest alkaline-earth metal that has similar chemical properties to barium.

After radium was discovered, it sparked the interest of many great scientists. Significant contributions to the research of radium, and to the development of radiochemistry, were made by Daniel Strömholm and Theodor Svedberg. In 1909 they showed that ^{223}Ra co-precipitates isomorphically with $Ba(NO_3)_2$ and that isomorphism is of major importance in the separation of radioelements from solutions by precipitation. This fact was used to characterize some other elements of the thorium and actinium natural decay chains [STR09]. Radium-228 was investigated by Otto Hahn in 1907. He supposed that there was another radionuclide with a half-life of 5.5 years between ^{232}Th and ^{228}Th [HAH07]. Later he came to the conclusion that there were two of them: ^{228}Ac and ^{228}Ra [HAH08]. Fajans and Richter worked in a similar research area and in 1915 they combined the previously investigated rules of Fajans and Beer [FAJ13] and Paneth and Horovitz [PAN14] and formulated a rule of co-precipitation/adsorption, which is known as the rule of Fajans - Paneth [FAJ15]. In 1925 Otto Hahn and Lise Meitner provided a more detailed description of co-precipitation. They divided the process into two cases: participation of trace radioelements in the formation of the carrier solid phase crystal lattice (solid solution) and adsorption of radioelements on the carrier precipitate [HAH25]. Another pioneer in the research of radium chemistry was Vitaly Khlopin. Together with his co-workers, he carried out quantitative research of the radium and barium co-precipitation process and investigated the law of redistribution of trace components between liquid and solid phases (Khlopin's law) [KHL24, KHL38].

After radium was discovered it immediately found a wide range of more or less appropriate applications. Up to 20 kg of radium was separated from ores and minerals world-wide. Radium was available to the public in the form of bottled drinking water or pellets and was also used as a radioluminous material in watches and paints [ROW95]. However, in the 1930s it was recognized that radium was among the most toxic elements and later approximately 85 % of all radium produced was used in medicine, mostly as an external radiation source in brachytherapy [VDO73]. At the end of the 20th century radium was replaced by reactor-produced nuclides. After that time these high dose radium sources were no longer used and needed to be stored in a specially equipped nuclear facility or disposed of in a nuclear waste repository. Radiochemistry as a part of both science and industry began with radium.

Radium isotopes are part of the uranium (^{238}U, ^{235}U) and thorium (^{232}Th) natural decay chains. Therefore radium is a Naturally Occurring Radioactive Material (NORM) because it is always present in uranium and thorium ores and minerals in secular equilibrium as a primordial radionuclide. Radium has no stable isotopes and due to the long half-life of 1600 years and the relatively high abundance of the parent nuclide (^{238}U) ^{226}Ra is the most abundant radium isotope.

Nowadays radium is of interest from an environmental point of view because together with its daughter radon, as NORM radionuclides, are the main components of public exposure, sometimes accounting for half the total exposure from all sources [WAT05]. Radium can be leached from uranium ore, for instance by rainwater, and migrate to drinking water and soil. From the soil it can be taken up by plants. On the other hand, migration allows the use of radium as a tracer for the investigation of processes which occur in nature, especially in groundwater [POR08]. In subterranean waters in Sweden, ^{226}Ra activity can reach the level of 2.5 Bq/L [SSI96], and 17-27 mBq/g in some Brazil nuts [PAR08].

Radium can present a high risk for the environment and humans when it is concentrated in man-made activities. In this case it is defined as a Technologically-Enhanced, Naturally-Occurring Radioactive Material (TENORM). The undesirable concentration of radium as a TENORM occurs in several human activities; uranium mining [CAR07, TRI08], phosphate mining [HAR01, BAR92], coal and metal mining [IAEA03], coal combustion [BAX96, HEX11], peat combustion [HED92], oil and gas production [EXP87, ALM07, HEL00], used nuclear fuel [IAEA90, SKB06, SKB11] and others.

The concentration of radium in different human activities and its migration from solid natural sources and man-made wastes leads to a strong interest in environmental science. To be able to model these processes, reliable thermodynamic data of radium compounds (solubilities, complex formation, co-precipitation etc.), preferably experimental [LOW85], are needed.

2. Background

2.1 Solubility of radium sulfate: available literature data

The solubility of radium sulfate was first experimentally determined by Lind and coworkers in distilled H_2O for a wide range of H_2SO_4 concentrations and 0.1 M Na_2SO_4 [LIN18]. A significant rise in solubility was observed with H_2SO_4 concentrations above 11.5 M. Later Erbacher [ERB30] carried out experiments to determine $RaSO_4$ solubility in H_2O and the solubilities that were determined were considerably higher than those of Lind. It was supposed that the low solubility obtained by Lind and coworkers was due to absorption losses of radium on glass and during filtration. Later, the results of both Lind and Erbacher were called into question by Nikitin and Tolmachev [NIK33], who made a careful study and prevented adsorption of radium by pre-equilibration of filters and pipettes with the radium stock solution. Radium adsorption on some other glass dishes was avoided by adding magnesium as a carrier. Both filtration and centrifugation were used for phase separations and led to similar solubility values. Data from [NIK33] include $RaSO_4$ solubility determination in pure water and diluted Na_2SO_4 at 20 ºC. Recently another experimental determination of $RaSO_4$ solubility was done in 0.02 M $NaSO_4$ solutions at 30, 50 and 70 °C [HED13] at pH 3 and the experimental values obtained were in good agreement with data from both Nikitin and Tolmachev [NIK33] and with theoretical models [LAN85, BRO15].

Taking into account these facts, only data for $RaSO_4$ solubility from some sources [HED13, NIK33] can be considered as reliable. Both data sets include $RaSO_4$ solubility in pure water or in dilute Na_2SO_4 solutions. As discussed earlier [PAI98], there are some additional difficulties for solubility determination in water and in dilute solutions (e.g. surface poisoning). It is also known [BUC04] that alkaline-earth metals, including radium, form relatively strong ion pairs with the sulfate ion. A background, inert electrolyte was not used in these studies to maintain a constant ionic strength, and therefore, extrapolation to zero ionic strength is problematic and some assumptions have to be made. The available accepted experimental data for $RaSO_4$ solubility are listed in Table 2.1.

Table 2.1 Literature experimental data for $RaSO_4$ solubility

$[Ra]^{total}$, M	$[SO_4]^{total}$, M	Apparent pK_{SP}	Media	Temperature, K	Note	Reference
$1.07 \cdot 10^{-6}$	$5.1 \cdot 10^{-5}$	10.26	$5 \cdot 10^{-5}$ M Na_2SO_4	293	filtration	[NIK33]
$1.45 \cdot 10^{-7}$	$5 \cdot 10^{-4}$	10.14	$5 \cdot 10^{-4}$ M Na_2SO_4	293	filtration and centrifugation	[NIK33]
$3.06 \cdot 10^{-8}$	$5 \cdot 10^{-3}$	9.82	$5 \cdot 10^{-3}$ M Na_2SO_4	293	filtration and centrifugation	[NIK33]
$6.52 \cdot 10^{-6}$	$6.52 \cdot 10^{-6}$	10.37±0.02	distilled H_2O	293	Average (5 experiments), crystallized $RaSO_4$	[NIK33]
-	$2 \cdot 10^{-2}$	10.52	$2 \cdot 10^{-2}$ M Na_2SO_4	283	-	[HED13]
-	$2 \cdot 10^{-2}$	10.38	$2 \cdot 10^{-2}$ M Na_2SO_4	293	-	[HED13]
-	$2 \cdot 10^{-2}$	9.95±0.1	$2 \cdot 10^{-2}$ M Na_2SO_4	303	-	[HED13]
-	$2 \cdot 10^{-2}$	9.89±0.12	$2 \cdot 10^{-2}$ M Na_2SO_4	323	-	[HED13]
-	$2 \cdot 10^{-2}$	9.71±0.1	$2 \cdot 10^{-2}$ M Na_2SO_4	343	-	[HED13]

2.2 Solubility of radium carbonate: available literature data

To the best of our knowledge, the solubility of $RaCO_3$ has never been determined experimentally. Langmuir and Riese [LAN85] estimated a –log K_{sp} for $RaCO_3$ at ambient temperature and pressure using an electrostatic approach and obtained a value of 8.3. Experiments on the precipitation of pure $RaCO_3$ and $BaCO_3$ were carried out by Nikitin [NIK37]. Radium and barium were precipitated separately at high pH by addition of equal amounts of $(NH_4)_2CO_3$ and NH_4Cl. It was found that the concentration of radium in solution after precipitation is approximately one order of magnitude higher than the concentration of barium in another solution. Based on this fact Nikitin supposed that solubility of $RaCO_3$ is approximately ten times higher than the solubility of $BaCO_3$.

2.3 Methods for conversion of solid radium sulfate into aqueous solution

As was mentioned before radium is used in medicine. Sealed ^{226}Ra sources, often in the form of the sparingly soluble sulfate salt, were widely used in radiation therapy, especially brachytherapy [SCI18, KJE63]. At the end of the 20th century radium was replaced by reactor-produced nuclides. Nowadays, according to the available information from the NEA/OECD [NUC15] ^{99m}Tc is used in more than two thirds of all diagnostic medical isotope procedures in the world. There are two basic methods of ^{99}Mo production in nuclear reactors; reaction of ^{235}U fission and reaction of ^{98}Mo neutron capture. As previously shown [MAT13, RYA04] the ^{98}Mo neutron capture reaction can be used in reactors with high resonance neutron flux to produce ^{99m}Tc generators and significantly reduce the amount of nuclear waste.

The production of $^{226}RaSO_4$ from these sources can be of interest from a scientific point of view because it is the only long-lived radium isotope with a half-life of 1600 years and can be used to study radium solution chemistry. As was also previously shown [KAR72, KUZ12, BAG15, KUK15], ^{226}Ra can be used as an irradiation target in a nuclear reactor to produce a high specific activity $^{227}Ac/^{223}Ra$ generator via the $^{226}Ra(n,\gamma)^{227}Ra$ neutron capture reaction. For safety reasons these radium sources are usually produced in the form of $RaSO_4$ powder, which is sealed in e.g. platinum cylinders inserted into various types of steel holders or holders made from other metals. $RaSO_4$ has extremely low solubility in water and aqueous solutions of mineral acids or alkali and in the case of leakage from a metal holder will not be as harmful to man and the environment as other radium compounds.

Thus, disassembly of old ^{226}Ra sources and conversion of $^{226}RaSO_4$ into aqueous solution may be of interest both for irradiation targets for radiopharmaceutical production of $^{223}RaCl_2$ and for scientific purposes.

The recommended value for the logarithm of the $RaSO_4$ solubility product at 298 K is -10.21 [BRO15]. Due to the low solubility of the $RaSO_4$ the use in e.g. solution chemistry investigations or as an irradiation target for $^{227}Ac/^{223}Ra$ generators is challenging. In the literature several methods have been suggested. In principle any method suitable for $BaSO_4$ dissolution is also useful for $RaSO_4$ due to the chemical similarity of $BaSO_4$ and $RaSO_4$. However, the fact that radium has no stable isotopes introduces some experimental limitations. Lind and coworkers observed a significant increase in $RaSO_4$ solubility at high H_2SO_4 concentrations (above 11.5 M) [LIN18]. It can be supposed that at such high concentrations of H_2SO_4 a negatively charged radium complex is formed. This method is inconvenient for the conversion of $RaSO_4$ into soluble form because when the solution is diluted, a $RaSO_4$ precipitate will be formed again [KUZ13]. Several methods were evaluated in the early 20th century. One of these methods was the reduction of $RaSO_4$ to RaS by ignition with calcium carbide, calcium hydride and carbon and subsequent dissolution of RaS [EBL13]. Another method was the conversion of $RaSO_4$ into soluble $RaCl_2$ and included heating $RaSO_4$ to 650 ºC in a mixture of gaseous CCl_4 and HCl [WHY12]. As has also been shown [BRE15], $RaSO_4$ can be directly converted into $RaCO_3$ by fusion with alkali metal carbonates. Nowadays these methods are deemed unsuitable from a radiation protection point of view due to high temperatures and the need for oxygen-free atmospheres in the case of the reduction to sulfide.

As has been shown [ALA16], a $Ra(Ba)SO_4$ precipitate can be also reduced to Ra(Ba)S at room temperature using $NaNO_2$ and thus can be dissolved in mineral acids. In this case high concentrations of acids and reducing agents are required to convert more than 90 % of $Ra(Ba)SO_4$ into aqueous solution. At room temperature and atmospheric pressure $RaSO_4$ can also be dissolved using chelating agents. Vebersik and Horovǎ used 5 % $(NH_4)_2EDTA$ solution to dissolve $RaSO_4$ [VEB58II]. Kuznersov and co-workers [KUZ13] used 100 ml of 5 % Na_2EDTA with 0.03 M NaOH to dissolve about 10 mg of $RaSO_4$. After dissolution, saturated Na_2CO_3 and 2 M $Pb(NO_3)_2$ were added to the solution to decompose the radium-EDTA complexes and precipitate the radium in the form of $RaCO_3$. After 1-2 hours of ageing, the $RaCO_3$ precipitate was filtered, washed with 0.01 M Na_2CO_3 and dissolved in 0.5 M HNO_3. According to the authors it was possible to recover 90.9 % of the radium using this procedure.

$RaSO_4$ can also be dissolved using ion exchange resins. The dissolution process is usually slow, but reaction kinetics can be increased by e.g. a temperature increase, stirring, use of fine bead resins or periodic solution acidification [OSB53, BOK84]. Dedek [DED60] used a mixture of cation and anion exchangers in H^+ and OH^- forms to dissolve 10 mg of $Ra(Ba)SO_4$ at 60 ºC. Under these conditions the dissolution process was fast and took 30 minutes.

One of the first methods for $RaSO_4$ dissolution was investigated by Marie Curie [CUR10]. Her method included heating solid $RaSO_4$ in concentrated Na_2CO_3 to 80-100 ºC and thus radium precipitated as $RaCO_3$, which can be dissolved in mineral acids.

Recently, many different methods for $BaSO_4$ as a substitute for $RaSO_4$ dissolution have been tested experimentally, but only methods with Na_2CO_3 and alkaline solution of Na_2EDTA have resulted in high barium dissolution yields (more than 90 %) [KOZ15]. The method with Na_2EDTA included $BaSO_4$ heating to 85 ºC in three-fold Na_2EDTA excess for 30 minutes. In the case of the method using Na_2CO_3 the solution was heated using either a heating plate or microwave power. It was found that in the case of microwave heating the conversion of $BaSO_4$ into $BaCO_3$ was faster and could be carried out in more dilute Na_2CO_3 solutions, while keeping the same yield. More than 90 % radium yields were obtained in the case of a Na_2CO_3:$BaSO_4$ molar ratio of 86 (normal heating) and 16 if microwave dissolution was used [KOZ15]. However, microwave dissolution requires special equipment, which when working with $RaSO_4$ will be contaminated. The methods outlined above are summarized in Table 2.2. In addition to the issues mentioned above, any work with radium is always done in hot cells or glove boxes, where space is limited.

It can be concluded that the Curie method is the most appropriate for obtaining high purity dilute aqueous radium solutions.

Table 2.2 Methods for $RaSO_4$ conversion into aqueous solution

Method	**Reference**
Reduction to RaS at high temperatures and oxygen free atmosphere	[EBL13]
Conversion into halides at 650ºC	[WHY12]
Fusion with alkali metal carbonates	[BRE15]
Reduction to RaS at room temperature using $NaNO_2$	[ALA16]
Ion exchange	[DED60]
Curie method (conversion into $RaCO_3$ in solution at elevated temperatures)	[CUR10, KOZ15]
Dissolution using chelating agents	[VEB58I, VEB58II, KUZ13, KOZ15]

3. Theory

According to the electron configuration of radium only one stable oxidation state (+2) is possible and no other stable states were experimentally determined by Hevesy [HEV13]. Among other natural alkaline-earth metals, Ra^{2+} has the lowest tendency to form complexes due to the large ionic radius. According to Shannon [SHA76] the effective ionic radius of radium is 1.48 Å in 8-fold coordination and 1.7 Å for 12-fold coordination.

Radium(II) forms strong complexes mostly with organic ligands [VDO73, SCH50] and the stability constants for strong complexes ($K° > 1000$) are usually relatively easy to determine experimentally [ROS61, SCH61, ROS74, CON87, BEC90, MAR92]. There is a huge set of data of experimentally determined stability constants for strong complexes of various compounds and it is always necessary to review the data critically including experimental methods and mathematical evaluation before accepting any value of the stability constant [MAR74]. Recently several thermodynamic databases were developed by teams of different experienced chemists who critically reviewed and compared the available stability constants: e.g. NAGRA, NEA-TDB, NIST, OECD and others. Another important aspect in determining the stability constant, except its validity, is estimation of uncertainties of the given stability constant [EKB99].

Different estimation approaches for the thermodynamic properties of radium, including complex formation and solubility, are widely used. One of the most widely used approaches to derive radium compound thermodynamic properties, for example stability constants or ion interaction coefficients, is the electrostatic model. The model is based on linear regression of radium thermodynamic properties from the experimental data for the same thermodynamic property of other alkaline-earth metals with the same coordination number against ionic radii of radium and other alkaline earth metals [LAN79, LAN85, LOW85, ROS11, PAI98]. As a result a predictive value for radium thermodynamic properties can be obtained, but some deviations can also be expected. The molar mass of radium is much higher than for the other alkaline-earth metals. As a result relativistic effects can occur (for more details about relativistic effects, refer to [THA10, PIT79] and references therein). Therefore, experimental determinations of radium thermodynamic properties, including stability constants for aqueous radium complexes with inorganic ligands, solubility constants and activity coefficients are important not only for the environmental science but also for validation of the theoretical models.

3.1 Activity coefficients

The laws developed for ideal solutions (and also ideal gases) are not valid for real thermodynamic systems, even at moderate concentrations. The deviations can be explained both by incomplete dissociation of “strong” electrolytes and partial weak complex formation and by specific ion interactions (activity coefficients). Activity coefficients are important because any experimental stability constant determined at a particular ionic strength (e.g. in 1

M of NaCl) is not of much use because it is valid only for this ionic strength and only for this electrolyte. Therefore stability constants are usually determined at different ionic strengths of the same electrolyte (different concentrations) and then extrapolated to zero ionic strength.

The fundamental theory about activity coefficients was investigated by Debye and Hückel [DEB23] who proposed that the deviation of strong electrolytes from ideality at low concentrations is connected with long-range electrostatic interactions of ions and can be derived using the Debye-Hückel limiting law which can be used to calculate activity coefficients of strong electrolytes up to an ionic strength of approximately 0.001 M:

$$\log(\gamma_i) = -A \cdot z_i^2 \cdot \sqrt{I} \qquad 3.1$$

The model was extended and became valid up to approximately 0.1 M ionic strength for strong 1-1 electrolytes and the extended Debye-Hückel law was derived (derivations for both 3.1 and 3.2 and other details can be found in [KOR93]):

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} \qquad 3.2$$

where γ_i is the activity coefficient of an ion and

A – temperature and pressure dependent constant;

z_i – ion charge;

I – ionic strength, function of concentration and charge of all electrolytes in the solution;

B – temperature and solvent relative permittivity dependent constant; and

a – distance of closest approach or effective Debye-Hückel ionic radius.

Davies [DAV62] added another term to the extended Debye-Hückel law and the applicability increased up to approximately 0.2 M ionic strength:

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + \sqrt{I}} - 0.15 \cdot I \qquad 3.3$$

Later Brønsted introduced a specific interaction of ions principle and derived the Specific Ion Interaction Theory (SIT) [BRO22], which was further developed by Scatchard [SCA36] and Guggenheim and Turgeon [GUG55]:

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + \sum_{n=1}^{s} \varepsilon_{i-j} \cdot I \qquad 3.4$$

where ε_{i-j} is the specific ion interaction coefficient between ion *i* and the oppositely charged ion of the background electrolyte *j*.

The first term in Eq. 3.4 is essentially the extended Debye-Hückel law and therefore is called the Debye-Hückel term. The value of $B \cdot a$ is usually fixed to 1.5 (for a detailed discussion refer to [GRE13]), but some authors do not recommend doing this [MAR06b]. As mentioned before, the Debye-Hückel term represents non-specific long-range electrostatic interactions of ions. Accordingly, it is supposed that the second term takes into account specific short-range interactions of ions. The nature of these short-range interactions is a subject of discussion. It is supposed that the second term takes into account solvation of an ion with solvent molecules and thus depends on solvent permittivity [KOR93]. Other effects probably also take place.

In the SIT, ion interaction coefficients for ions of the same charge, neutral species, ion triplets and others are neglected. The idea of the SIT, as pointed out by Jannik Bjerrum, is that at ionic strengths higher than 0.1 M activity coefficients depend not only on the ionic strength itself but also on the concentration of all ions and ligands in the solution [BJE89]. The SIT can be applied up to ionic strengths of about 3.5 M.

Later Ciavatta [CIA80] added a second ion interaction coefficient and extended the SIT to be applicable at higher ionic strengths:

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + \sum_{n=1}^{s} \left(\varepsilon_{i-j}^1 + \log \varepsilon_{i-j}^2 \right) \cdot I \qquad 3.5$$

where ε_{i-j}^1 and ε_{i-j}^2 are the first and second specific ion interaction coefficients between ion *i* and the oppositely charged ion *j* of the background electrolyte, respectively. The extended SIT model was criticized later [GRE13] because:

$$\left(\varepsilon_{i-j}^1 + \log \varepsilon_{i-j}^2 \right) \rightarrow -\infty \text{ when } I \rightarrow 0 \qquad 3.6$$

As a result another model [ALL97] was proposed [GRE13]:

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + \sum_{n=1}^{s} \left(\varepsilon_{i-j}^1 + \varepsilon_{i-j}^2 \cdot \sqrt{I} \right) \cdot I \qquad 3.7$$

However, the criticism of Eq. 3.5 by [GRE13] is unfounded because the limit of the second term, because it is multiplied by *I*, approaches zero as the ionic strength approaches zero.

A more complicated model for ion activity coefficient calculations at high ionic strength (in some cases up to saturation) was derived by Pitzer and co-workers by analogue with equations of real gases [PIT73, PIT91, PIT95]. Later it was shown that the Pitzer formalism can be used to predict mineral solubilities in sea water [HAR80]. A comparison of the Pitzer and SIT models has been made by many authors [ELI95, GRE97a].

Pitzer and SIT are assigned to ion interaction models because in both models it is assumed that strong electrolytes are completely dissociated, and sometimes it is not an easy task to distinguish between strong and weak electrolytes. If there is some reliable evidence from the literature that an electrolyte forms ion pairs then SIT or Pitzer models have to be modified to include weak complex formation. For example, the fact that some 2-2 electrolytes (e.g. alkaline-earth metals and sulfate ions) form ion pairs in aqueous solution was recognized by Pitzer and Mayorga [PIT74] and the model was modified.

However, the main drawback of both the Pitzer and SIT models is that both are semi-empirical and thus activity coefficients of an ion for any particular system can be calculated only if experimental data for the ion interaction parameters are available. Nowadays the Pitzer formalism is widely used in geochemistry, probably because more ion interaction parameters are available in the literature for the Pitzer model than for the extended SIT.

Investigation of the theoretical model that could be used to accurately compute activity coefficients of ions at various conditions (high ionic strengths, temperatures, pressures, different solvents etc.) is a great challenge and requires a fundamental understanding of the nature of the “specific interactions” and reasonable mathematical models to describe such interactions. Such a model has not been investigated yet and therefore there are several experimental methods that are used to derive ion interaction parameters and determine activity coefficients [KOR93]:

1. Change of *vapour pressure* of pure solvent and with solute;
2. Change of *boiling point* of pure solvent and with solute;
3. Change of *freezing point* of pure solvent and with solute;
4. Isopiestic measurements of osmotic coefficients;
5. Electromotive force (emf) measurements; and
6. Solubility measurements.

To the best of our knowledge, the experimental determination of radium activity coefficients or ion interaction parameters has never been reported, probably because it has no stable isotopes and such measurements require rather high concentrations and will thus also be highly radioactive and produce significant amounts of radon. Also, radioactive contamination of equipment is undesirable.

Due to the lack of experimental data, extrapolation of ion interaction parameters of radium from the values of other alkaline-earth metals using ionic radii or using interaction parameters of barium directly are the methods used to calculate radium activity coefficients [PAI98, ROS11]. Experimental determination of radium ion interaction parameters could contribute to the solution chemistry of this element and extend our knowledge in this area. Probably, the solubility of sparingly soluble radium salts is the most reasonable method for the determination of its activity coefficients.

3.2 Weak complex formation

To the best of our knowledge, there is no reliable experimental study of radium complex formation with inorganic ligands. This fact can be explained by the difficulties of determining experimental weak complex stability constants and data evaluation. Weak complex formation, sometimes referred to as ion association or ion pairing, is a special case of equilibrium. A review defining the "state of the art" by Marcus and Hefter [MAR06b] throws light on what has been done for the past 130 years in the area of weak complex formation. Theoretical methods of experimental data analysis developed for strong complexes are not valid for weak complexes. This is due to the fact that in the case of weak complex formation it is necessary to substitute significant amounts of background electrolyte (more than 10 %) with the complexing agent to be able to detect any weak complex formation.

It is also usually required to go to high ionic strengths, because complexes can start to form only at high ligand concentrations (3 M in some cases or even higher). Thus, it becomes necessary to distinguish between two effects; weak complex formation (short-range interactions between two oppositely charged ions) and activity coefficient changes (specific ion interaction effects). This is not a trivial task and in some cases one of the effects is neglected even by experienced researchers, leading to incorrect results [ZIE05, MAZ65, ALN70]. These two effects can be distinguished either by quantitative measurements of the weak complexes formed or by measurements of the activity coefficient changes with a change of solution composition. The concept of ion pairing was developed by Eugen and Tamm [EIG62a, EIG62b]. According to the mechanism there are three types of ion pairs; solvent separated, solvent shared and contact ion pairs. The experimental methods used for studying weak complex formation include conductivity and spectroscopic measurements (UV, IR, NMR, Raman, relaxation etc.). Some methods (e.g. ultrasonic, dielectric relaxation spectroscopy) allow distinguishing between different types of ion pairs [MAR06b]. It can be shown that some electrolytes, which were recently considered as completely dissociated (e.g. Na_2SO_4 or $Ba(OH)_2$), form ion pairs in aqueous solution [DAL72, DAN08, BRO16].

These methods are difficult to apply in studying radium weak complex formation for the same reasons as was the case in the experimental determination of radium activity coefficients. For example, the minimum concentration of radium required in solution in the case of conductivity measurements is 0.5 mM.

It is necessary to use ion association models if weak electrolytes occur in solution at relatively high concentrations. Bjerrum [BJE26] was the first to develop the model that takes ion pairing into account. More advanced models include the low concentration chemical model (lcCM) [BAR79] and the mean spherical approximation model (MSA) [KRI98] (for more detail refer to [MAR06b]). Another possibility is to combine ion association and ion interaction approaches. For example, Whitfield extended the Pitzer model by implementing ion association equilibria [WHI75].

If relatively significant amounts of ion pairs, complexes or other uncharged species are formed then it is also necessary to include their activity coefficients into models because of the dipole moment. Activity coefficients of uncharged species can be computed using the Sechenov empirical model:

$$\log(\gamma_{ip}) = K_s \cdot I \qquad 3.8$$

where K_s is the empirical Sechenov coefficient and I is ionic strength. Later the model was modified by Reardon and Langmuir to fit experimental data for $MgCO_3°$ and $CaSO_4°$ activity coefficients at moderate ionic strengths [REA76]. Other models based on salting in and out effects and on analogy with zwitterions have also been proposed [MAR06a]. The activity of water is another term that is sometimes neglected but should be considered if water is involved in the equilibrium (for more detail, refer to [BRO16, GRE13]. It can also be pointed out that in some cases triple, quadruple or other polynuclear complexes are formed. In these cases careful data analysis is required to obtain information about these complexes [BUC04].

Moreover, Marcus and Hefter [MAR06b] pointed out other problems of weak complex formation that have not been solved yet. This includes the problem of choosing the distance at which free ions have to be considered as associated, the problem of the minimum value of a weak complexation constant, which can be determined experimentally, and many others.

3.3 Experimental determination of solubility of sparingly soluble compounds in aqueous solutions

Determination of the solubility of sparingly soluble salts is a separate field of science. Because of the importance, theoretical fundamentals and experimental difficulties in determination of solubilities have been the subject of review papers [ZIM52, JOH68, NIT91, HEF13] and also recently published books [HEF03, ZEM10]. Surprisingly few articles also include a detailed discussion of the experimental problems [PAI98].

As was pointed out, to be able to model activity coefficients accurately and extrapolate solubility product constants to zero ionic strength it is necessary to maintain constant ionic strength. This can be done by addition of a strong, inert electrolyte (e.g. $NaClO_4$, NaCl).

In solubility studies it is necessary to have both solid and liquid phases in full contact [HEF03]. This can be achieved by shaking or stirring the samples.

One of the basic questions in the determination of solubility constants is if equilibrium has been reached. Ideally, solubility experiments are done by approaching equilibrium from both under- and over-saturation, and if the obtained constants are within the experimental uncertainty then it can be supposed that thermodynamic equilibrium has been reached. However, in some cases it is difficult or not possible to synthesize and prepare the same solid compound for undersaturation studies. On the contrary, it may be impossible to precipitate the same solid studied using undersaturation, from oversaturation. In this case one could rely on literature data of the experimental equilibration time for the same or a similar compound. Another possibility is to carry out solubility experiments at different conditions (change background electrolyte, temperature, pressure etc.) to obtain as many experimental points as possible. If the obtained experimental results give the same solubility constant or follow well-established laws, then it can be supposed that equilibrium has been reached. As was pointed out by Nitsche [NIT91], the question about evidence of equilibrium can be always raised. He preferred the term “steady-state” instead and pointed out that “steady-state thermodynamic forces may still change the solution composition: solids become less soluble as they change from a higher to a lower energy. The change may be very slow and may not be evident in experiments even after several years”.

It is necessary to study solubility from under- and over-saturation using the same solid compound because particle size and crystal structure is of major concern in solubility studies. Amorphous solids are usually more soluble than crystalline solids of the same chemical composition [NIT91]. The effect of particle size on the solubility of sparingly soluble compounds was discussed in detail by Paige and co-workers [PAI98] and others [HEF03] and it was pointed out that particles of 0.4 µm in diameter can give a significant rise in solubility. As a result, the solid precipitated from an over-saturation study or the solid synthesized from an undersaturation study has to be carefully characterized using different techniques (e.g. XRD, SEM etc.) if possible.

In solubility studies it is usually necessary to completely separate solid and liquid phases and this can be problematic, especially if colloids are formed. Filtration and centrifugation are the most widely used methods. The main problem is adsorption losses on filters, centrifuge tubes or other materials (pipette tips etc.), which can lead to significant decreases in apparent solubility. As was shown [NIK33], this was the main source of the error in the first two experimental determinations of radium salt solubilities. Therefore, adsorption of Ra^{2+} from very dilute aqueous solutions and pure water on different materials has been studied experimentally by several researchers [STA37, TSE86] and reviewed [VDO73]. It was shown that for Ra^{2+} behaviour in dilute aqueous solution corresponds to typical adsorption phenomena and that Ra^{2+} sorption on glass occurs at a pH higher than 2 [STA37].

There are several methodologies that can be used to minimize sorption effects. One possibility is addition of barium as a carrier when possible [VDO73]. Tsezos and co-workers, among others [TSE86], recommend use of Teflon as the non-adsorbing material. If the sample volume is large enough then it is possible to take several samples and filter them using the same filter, as for example Nikitin and Tolmachev did [NIK33]. After that the concentration of radium can be measured in the filtrate after each filtration step. If the value of the concentration is constant then it can be supposed that adsorption has not occurred. If the concentration increases after each filtration step then one can discard the first values and take only the last values when the radium concentration becomes constant.

After the separation of liquid and solid phases it is necessary to measure the concentration of ligand and/or metal ion. Sometimes it is possible to measure the free ligand and/or free metal ion concentration using for example emf. But if such measurements are not possible then it is necessary to have reliable data on the complexation of the free metal ion with other ligands. For example at relatively high pH hydrolysis of the radium ion can occur and if for example gamma spectrometry is used, then total concentration of the metal ion will be measured. Then it becomes necessary to calculate the concentration of the free radium ion and the concentration of the hydrolyzed radium ion using hydrolysis stability constants. For many metal ions reliable hydrolysis constants can be found in a recently published book [BRO16]. In the case of radium emf measurements are difficult, but on the other hand it might be mentioned that it is fortunate that radium has no stable isotopes and can be easily measured with high sensitivity using its gamma emissions using a HPGe detector.

In some cases when experimentally determining solubilities it is necessary to maintain high pH. In principle CO_2 can be absorbed by the sample if it is exposed to air for a long time. The process of CO_2 absorption consists of several stages; diffusion of CO_2 from the air to the interphase, diffusion of CO_2 into solution through the interphase, CO_2 solvation and reaction of solvated CO_2 with water according the reaction:

$CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^-$

As can be observed, the pH of the sample will be decreased. However, diffusion is the limiting stage of the process and this is very slow. Therefore it can be supposed that if a concentrated solution of NaOH or other hydroxides are not used, then the pH of the sample will be constant.

Paige and co-workers [PAI98] discussed the results of Bovington [BOV65], who studied the solubility of sparingly soluble $BaSO_4$ using inactive $BaSO_4$ and $^{135}BaSO_4$ and found that the solubility of radiolabeled compound is 10 % greater than the solubility of the inactive compound. It was also claimed that the increase was independent of specific activity. Later these results were called into question by Berdonosov [BER73], who obtained values for the solubility of inactive and radiolabeled $Ce_2(C_2O_4)_3$ within experimental uncertainty. Even Paige and co-workers [PAI98] used $^{133}BaSO_4$ and obtained solubility constants that are in good agreement with other authors. Therefore, it can be supposed that radioactivity has no influence on solubility phenomena.

There are many other experimental difficulties in the determination of solubilities; oxidation state, surface poisoning due to the presence of impurities in the case of determination of solubility in pure water and others. These difficulties are not relevant for the experimental determination of the solubilities of radium sulfate and carbonate used in this work and detailed discussion of these problems can be found in the literature cited in this chapter.

4. Experimental

Due to the gamma decay of ^{226}Ra and the in growth of its daughters including ^{222}Rn, extensive radiation protection is required when working even with microgram amounts of radium. It must be handled in hot cells or in negative pressure glove boxes equipped with a radon capture system. An efficient radon capture system was previously developed [HED12] and used in this study. The system included three columns, filled with 25 g of silver-exchanged zeolite from Sigma-Aldrich (pellets 1.6 mm), connected in series to each other and to a vacuum pump (KMP 5.5 $l \cdot min^{-1}$). Dose rates were always monitored and external surfaces periodically checked for contamination by swipe tests.

In this work the gamma spectrometry was made using a digital spectrum analyzer (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 and 0.9 mm carbon epoxy entrance window). Both detectors were energy and efficiency calibrated using a mixed radionuclide reference solution (NIST traceable from Eckert and Ziegler, USA). The relative efficiency calibration for the Ortec detector for energies below 59.54 keV was done using a ^{241}Am solution. All gamma spectrometric measurements were evaluated using the Gamma Vision 7.01.03 software. Nuclide half-lives, gamma emission energies and photon emission probabilities were taken from the Decay Data Evaluation Project [DDEP].

A rotary tool (Proxxon FBS 240/E) was used to cut platinum-gold cylinders with $RaSO_4$.

A Bruker D8 Advance diffractometer equipped with a CuKα X-ray source and Bruker A100B36 low background, airtight XRD sample holder for small amounts of environmentally sensitive material were used to examine $RaCO_3$ samples.

Shaking machines (IKA Vibrax VXR basic) connected to a heated circulating water bath (Grant TC120) were used for the radium sulfate and carbonate solubility studies.

Samples were centrifuged using a Beckman Allegra 64R Benchtop refrigerated centrifuge with a fixed angle aluminum biocontainment F2402H rotor.

All uncertainties of the measurements and fitting are two sigma standard uncertainties.

4.1 Disassembly of old radium sources and conversion of radium sulfate into radium carbonate for subsequent dissolution in acid

The radium was contained in a G11 vaginal applicator irradiation source (Fig. 4.1). The applicators had previously been used at Sahlgrenska University Hospital, Göteborg, Sweden, for the treatment of uterine cervix carcinoma [KJE63]. The source was produced in the 1940s and was in the form of flat plaques made from stainless steel with cut-off upper corners. According to the certification five platinum-gold cylinders were sealed in the plaque. Each sealed cylinder contained 20 mg of $^{226}RaSO_4$ powder. An important difference in the radium source from the source described in [KJE63] is the presence of a small open 8 mm cylinder inside the larger sealed platinum-gold cylinder.

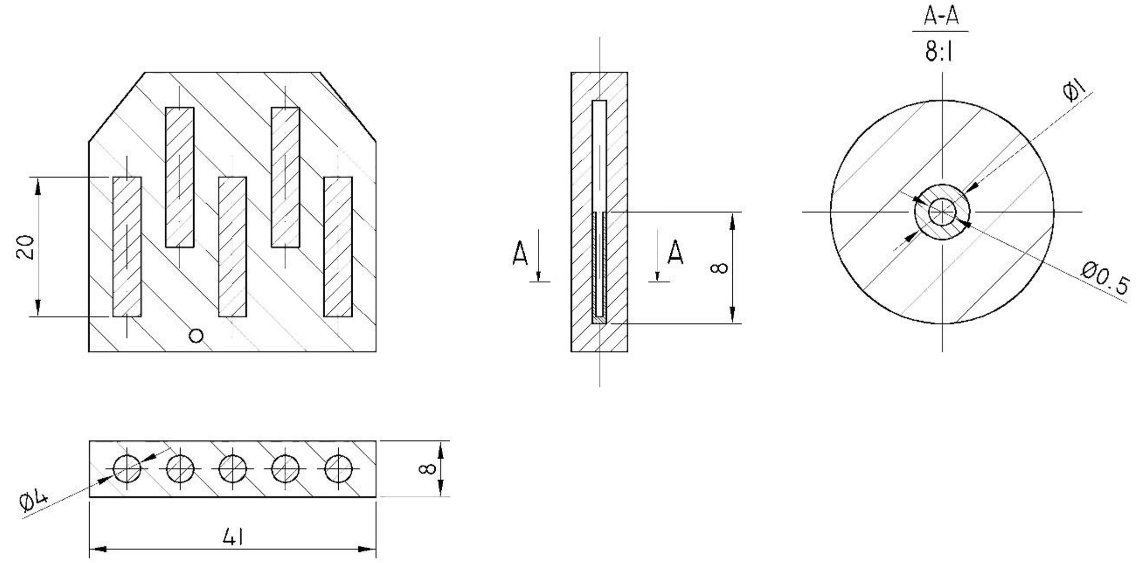

Figure 4.1 Radium source G11, all indicated distances in mm

Metal holders and platinum cylinders can either be dissolved in concentrated mineral acids, including aqua regia, or cut mechanically, for instance using a rotary tool. The mechanical method will lead to radium losses of at least 10 % [VEB58a]. The amount of lost $RaSO_4$ can be significantly reduced by dissolution of the platinum layer in aqua regia. Vebersik [VEB58a] described a procedure which allows radium to be separated from platinum, gold, silver and decay products of radium. Radium losses were 3-5 % compared to at least 10 % in the case of mechanical cutting of the platinum cylinder. Another advantage of chemical dissolution of radium cylinders is lower contamination levels of the glove box or hot cell areas, as all activity stays in solution. The choice of method depends on the thickness of the platinum layer of the cylinder. In the original paper [VEB58a] it was mentioned that it took only 1 hour to dissolve the platinum-iridium layer and therefore it can be concluded that the layer was very thin. It can be supposed that if the platinum layer is thicker than 0.1 mm the dissolution method will be extremely time-consuming and significant amounts of highly radioactive liquid waste will be formed.

The steel plaque was dissolved in 37 % HCl (Sigma-Aldrich ACS reagent) at about 50 °C inside a hot-cell. To speed up the process and avoid saturation of the acid, the acid was decanted and new acid added. This procedure was repeated three times until part of the steel was dissolved. Then the platinum-gold cylinders were taken out using tweezers and transferred into glass vials placed in lead containers for radiation protection. One of these containers was then transferred to a shielded glove box. The cylinders were cut mechanically from both sides using a rotary tool with a diamond cutting disk (Ø38×0.6 mm). Thereafter the small 8 mm cylinder was taken out into a glass vial by pressing with a drill. Almost all $RaSO_4$ powder was stuck inside the small cylinder and was taken out into the glass vial by moving a Ø0.4 mm drill inside the cylinder. The yellowish $RaSO_4$ powder thus obtained can be seen in Fig. 4.2.

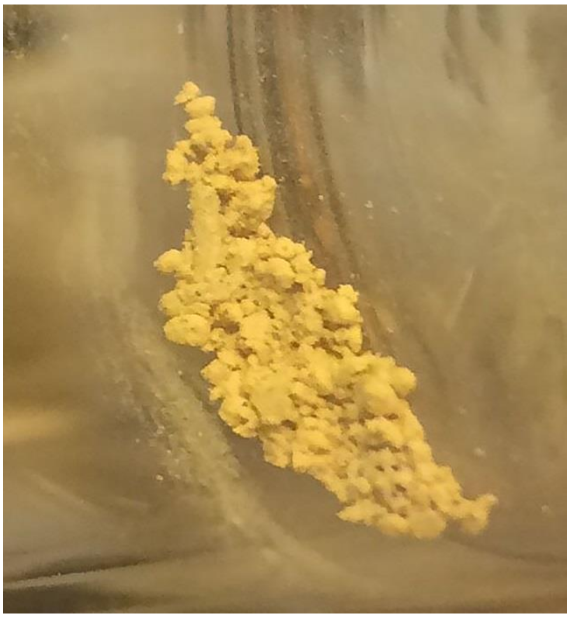

Figure 4.2 Radium sulfate powder

The $RaSO_4$ powder was then transferred from the glass vial into a 100 ml round-bottomed flask. The glass vial was rinsed three times with 1.5 M Na_2CO_3 prepared from solid anhydrous Na_2CO_3 (Fluka purum p.a. ≥ 99.0 %) and MQ water (18.2 MΩ.cm at 25 ºC, < 5 mg/l total organic content) to remove the rest of the $RaSO_4$ powder and the mixture of the rest of the solid $RaSO_4$ in Na_2CO_3 solution was added to the flask. A total volume of 14 ml 1.5 M Na_2CO_3 was added to the flask. A condenser was then connected to the flask and filled with 10 ºC water. The temperature in the condenser was controlled by a refrigerated/heating circulator Julabo FP50-HE connected to the flask. The flask with solid $RaSO_4$ and Na_2CO_3 solution was put in a heating mantle (electromantle Electrothermal EMA0250/CEB) at 85 ºC. After 90 minutes, heating was turned off and the solution was allowed to cool for 60 minutes.

In this method, sometimes referred to as the Curie method, radium is converted into carbonate according to the exchange reaction:

$RaSO_4(s) \rightarrow Ra^{2+}(aq) + SO_4^{2-}(aq)$

$Ra^{2+}(aq) + CO_3^{2-}(aq) \rightarrow RaCO_3(s)$

After cooling, the supernatant was removed using a Pasteur pipette and a second portion of 1.5 M Na_2CO_3 was added to the precipitate. The procedure was repeated two more times (three heating cycles in total) and after the third removal of supernatant the white $RaCO_3$ formed in the flask was washed with 25 ml MQ water three times.

This procedure was used two times to prepare two different portions of $RaCO_3$. One portion of the prepared $RaCO_3$ was dissolved in 7 ml of 2.77 M HCl prepared from Merck Suprapur® 30

% HCl and MQ water. Another portion was kept as solid $RaCO_3$. A small sample from the portion with solid $RaCO_3$ was put on mylar tape and attached to a non-diffracting substrate with airtight sample holder. The conditions for data collection were continuous scanning of a detector covering a 2Θ angular range from 10° to 60° with a step size of 0.01 and a wavelength of 1.542 Å.

For the determination of the radium concentration in the prepared solution, samples were taken after approximately two days and measured using the same geometry that a high purity germanium (HPGe) detector was previously calibrated.

4.2 Solubility of $RaSO_4$ and $RaCO_3$

Sodium chloride was used as a background, inert electrolyte because Cl^- is an omnipresent ligand in the environment and determination of radium solubilities at different concentrations of NaCl would give Ra-Cl ion interaction coefficients and contribute to environmental science. Another argument to carry out experiments in chloride media was that the radium stock solution consisted of 2.77 M HCl.

The amount of radium stock solution used was decreased to have as many experimental data points as possible by using Na_2SO_4 or Na_2CO_3 as a source for SO_4^{2-} and CO_3^{2-} ions, respectively. On the other hand it was necessary to keep the total ionic strength constant and therefore the ionic strength of NaCl was always more than approximately 80-90 % of the total ionic strength. It was also preferable to have some points at low ionic strength, therefore it was reasonable to keep the concentration of SO_4^{2-} at 10 mM in the case of $RaSO_4$ solubility and 100 mM of CO_3^{2-} in case of $RaCO_3$ solubility for all samples. The ionic strength of 10^{-2} M Na_2SO_4 and 10^{-1} M Na_2CO_3 is 0.03 M and 0.3 M, respectively, and this is relatively small when compared to the 0.3 M NaCl (when using sulfate) or 1.3 M NaCl (when using carbonate) as the background electrolyte.

As previously mentioned, the recommended value for the logarithm of $RaSO_4$ solubility product at zero ionic strength and 298 K based on experimental data [NIK37, HED13] is -10.21 [BRO15]. To the best of our knowledge the solubility constant of $RaCO_3$ has never previously been determined experimentally. Therefore, one possibility was to use the estimated value given by Langmuir and Riese [LAN85], who used the electrostatic approach to derive the logarithm of $RaCO_3$ solubility product constant at zero ionic strength and 298 K and obtained -8.3.

Apparent solubility product constants of alkaline-earth sulfates and carbonates at different ionic strengths are higher than the solubility at infinite dilution due to activity coefficients and/or complexation. An increase of apparent K_{sp} values from $K_{sp}°$ was estimated using data for the solubility of $BaSO_4$ and $BaCO_3$ in NaCl. A review of $BaSO_4$ solubility in NaCl media was undertaken by Monnin [MON99] and it was shown that at 5 M NaCl the solubility of $BaSO_4$ is approximately 2.5 orders of magnitude higher than the solubility at zero ionic strength. Careful experimental studies of the solubility of alkaline-earth metal carbonates in NaCl was done by Millero and co-workers [MIL84] and it was shown that at 5 M NaCl the solubility of $BaCO_3$ is approximately 2.1 orders of magnitude higher than solubility at zero ionic strength. Therefore, a 3.7 orders of magnitude increase of K_{sp} from the K_{sp} at infinite dilution in the case of the sulfate system and a 3.3 orders of magnitude increase of K_{sp} from the K_{sp} at infinite dilution in the case of the carbonate system was enough to keep radium samples oversaturated at all ionic strengths.

According to Goldberg and co-workers [GOL02], recommended IUPAC values for the H_2SO_4 and H_2CO_3 pK_a values (second dissociation step) at 298 K and zero ionic strength are 1.987 and 10.329, respectively. These values are in a good agreement with values given by Martell and Smith [MAR74]. Complete dissociation of H_2SO_4 and H_2CO_3 in NaCl media will occur at lower pH due to activity coefficient changes [GRE97b]. Therefore, it was supposed that at pH 4 and at pH 13 sulfuric and carbonic acids, respectively, will be completely dissociated.

Samples of 2 ml volume were prepared by dissolution of solid Na_2SO_4 (204447-10G Sigma-Aldrich ≥ 99.999 % trace metal basis LOT#MKBF8818V), solid Na_2CO_3 (451614-5G Sigma-Aldrich ≥ 99.999 % trace metal basis LOT#MKBQ0225V), solid NaCl (1.06406.0050 Merck Suprapur® ≥ 99.99 % B733806 616; 6000596344) in MQ water (18.2 MΩ.cm at 25 ºC, <5 mg/l total organic content). Radium stock solution was prepared from MQ water and HCl (Merck Suprapur® 30 %). The pH was adjusted using NaOH solution prepared from fixanal (38127-1EA Sigma-Aldrich LOT#SZBE2050V).

After preparation the samples were put inside sample holders on the top of shaking machines. A temperature of 25.1 ± 0.1 ºC was kept constant and the samples were gently shaken.

After some time, 100 µl samples were taken and centrifuged at 50000 G at 25.1 ºC for 1 hour. After that 10 µl samples were taken, pipetted into 1 ml of 4 M HCl and measured using an Ortec GEM-C5060 HPGe detector. The pH of all samples was roughly measured and for the sulfate samples it was in the range of 7-10 depending on ionic strength. In the case of the carbonate samples, the pH was higher than 13 for all samples.

5. Results and discussion

5.1 Disassembly of radium source

Samples of HCl in the end of the steel plaque dissolution were taken and measured using HPGe. The activity of ^{226}Ra in the sample was 21.4 Bq·ml^{-1}, which can be explained by probable $RaSO_4$ leakage from the platinum-gold cylinders [ROZ69] or contamination of the external surfaces. When two platinum-gold cylinders were cut mechanically and two small 8 mm cylinders were taken out, it was possible to obtain 34 mg $RaSO_4$ (20 mg $RaSO_4$ in each cylinder) using the procedure described above.

The second portion of prepared $RaCO_3$ was kept in solid form and studied using a X-ray diffraction (XRD) technique. The XRD pattern of the sample shows an amorphous structure for the $RaCO_3$ formed by the method used in this work. This result is in good agreement with the XRD data for $CaCO_3$ prepared in a similar way [KOG98, IHL14].

To the best of our knowledge, Weigl and Trinkl [WEI73] carried out the only experimental XRD study on crystalized $RaCO_3$. They reported a different $RaCO_3$ preparation procedure than used in this work. After $RaCO_3$ was synthesized it was dried at 150 – 200 ºC and then heated up to 640 ºC for 3.5 hours. According to the result and the literature, a further heat treatment step is necessary for crystallization of $RaCO_3$ for the proposed procedure.

It can be supposed that the $RaSO_4$ source used in this work was essentially free from any significant amount of barium. This statement is based on the results obtained by Hedström [HED13] who converted $RaSO_4$ from a source of the same origin into aqueous form and measured a sample of radium solution using inductively coupled plasma mass spectrometry (ICP-MS). According to the author the amount of barium in the sample was below the detection limit.

The dose rate from the prepared radium solution were approximately ten times lower than from the initial $RaSO_4$ powder, which indicates that radium was separated from its decay products. Three samples were taken from the prepared solutions and measured using gamma spectrometry (Canberra HPGe detector). The same samples were measured after approximately one year using the Ortec HPGe detector to measure the activity of ^{210}Pb. Identified nuclides and their activities with two sigma standard uncertainties are presented in Table 5.1.

Table 5.1 Identified nuclides in radium stock solution

Nuclide	Activity±2σ, Bq·µL^{-1}	Concentration±2σ, mol·L^{-1}
^{226}Ra	3320±140	$(4.0\pm0.2)\cdot10^{-4}$
^{214}Pb	68.4±3.6	$(2.6\pm0.1)\cdot10^{-13}$
^{214}Bi	70.2±3.9	$(2.0\pm0.1)\cdot10^{-13}$
^{210}Pb	227±21	$(3.8\pm0.4)\cdot10^{-7}$

^{214}Pb and ^{214}Bi are short-lived nuclides with a half-life of 26.9 and 19.8 minutes [DDEP], respectively, and therefore these indicate the presence of the long-lived mother nuclide ^{222}Rn (half-life 3.8 days). The activity of ^{226}Ra is significantly higher, which is in agreement with a dose rate decrease. This confirms that the radioactive equilibrium was disturbed and that ^{226}Ra was separated from its decay products during the dissolution procedure. The ratio between the molar concentrations of ^{210}Pb before the conversion of $RaSO_4$ into aqueous solution and afterwards is 0.07 ± 0.01, assuming that ^{226}Ra and ^{210}Pb were in equilibrium within the source, which indicates that 7 ± 1 % of the initial ^{210}Pb was co-precipitated with $RaCO_3$.

5.2 Solubility of radium sulfate

In can be supposed that NaCl is a strong electrolyte and is completely dissociated in aqueous solution, or the complex is so weak that it can be neglected. The concentration of SO_4^{2-} was maintained below 10 % of the total NaCl ionic strength in all test solutions. Therefore it can be concluded that the ionic strength was constant in all experiments and is equal to the concentration of NaCl. As was pointed out before, it is a well-known fact that alkaline-earth metals including radium as well as alkali metals such as Na^+ form ion pairs with sulfate and carbonate ions [BUC04, MAR06b, BUC99, DAL72]. Therefore the concentration of free radium $[Ra^{2+}]^{free}$ and free sulfate $[SO_4^{2-}]^{free}$ has to be computed. Concentrations of $[Ra^{2+}]^{free}$ and $[SO_4^{2-}]^{free}$ were computed from the measured and added concentrations of $[Ra]^{total}$ and $[SO_4]^{total}$ according to equations A10 and A16 (Appendix I), respectively. The fit together with ion interaction parameters and $[Ra^{2+}]^{free}$ at zero ionic strength obtained in a regression (equation A10) is shown in Fig. 5.1. The value of the $RaSO_4(aq)$ ion pair stability constant was taken from Langmuir and Riese [LAN85] as a first guess. This parameter affects only the first experimental point. In the case of $RaCO_3$ solubility, the $RaCO_3(aq)$ ion pair formation has no influence on the fitting parameters. After that, the apparent K_{sp} was calculated as a product of $[Ra^{2+}]^{free}$ and $[SO_4^{2-}]^{free}$. Ionic strengths of NaCl were recalculated from molar to molal using conversion factors taken from Silva and co-workers [SIL95]. The results are listed in Table 5.2. After that the solubility was extrapolated to zero ionic strength using equation A17 (Appendix I) (Fig.5.2).

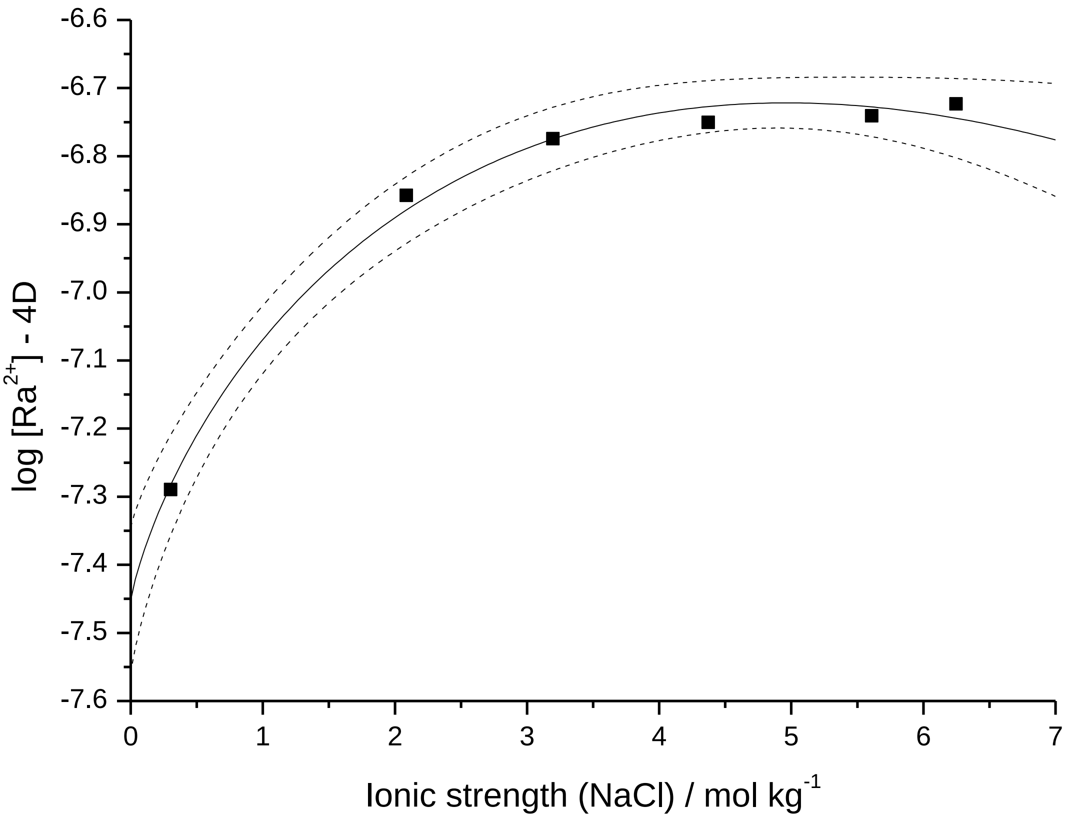

Figure 5.1 Extrapolation of log$[Ra^{2+}]^{free}$ to zero ionic strength using extended Specific ion Interaction Theory (equation A10 in Appendix I). The following parameters were obtained in a regression; log$[Ra^{2+}]^0$ = -7.45±0.11, $\varepsilon_1(Ra^{2+}-Cl^-)$ = -0.38±0.09, $\varepsilon_2(Ra^{2+}-Cl^-)$ = 0.34±0.1. The dotted lines are the 2-sigma (95 % confidence) lines.

Table 5.2 The results of radium sulfate solubility determination at 25.1 °C

Ionic strengths NaCl, mol·kg^{-1}	**$[Ra]^{total}$, M**	**Apparent logK$_{sp}$**
0.3	$(2.5 \pm 0.1)\cdot10^{-7}$	-8.85 ± 0.04
2.09	$(1.2 \pm 0.1)\cdot10^{-6}$	-8.02 ± 0.02
3.2	$(1.7 \pm 0.1)\cdot10^{-6}$	-7.83 ± 0.02
4.37	$(1.9 \pm 0.1)\cdot10^{-6}$	-7.75 ± 0.02
5.61	$(2.1 \pm 0.1)\cdot10^{-6}$	-7.69 ± 0.02
6.25	$(2.3 \pm 0.1)\cdot10^{-6}$	-7.66 ± 0.03

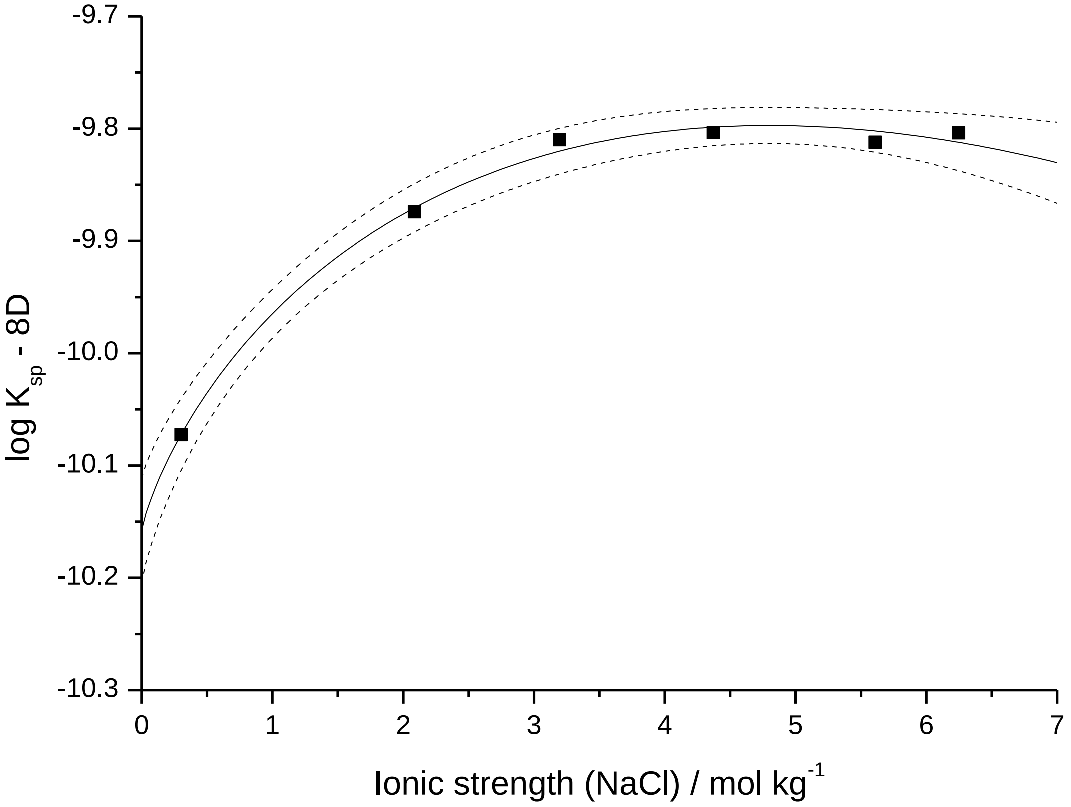

Figure 5.2 Extrapolation of logK$_{sp}$ of RaSO$_4$ to zero ionic strength using extended Specific ion Interaction Theory (equation A17 in Appendix I). The following parameters were obtained in a regression; logK$_{sp}^0$ = -10.16±0.05, ε_1(sp) = -0.19±0.04, ε_2(sp) = 0.34±0.05. The dotted lines are the 2-sigma (95 % uncertainty) lines.

The solid curve in Fig. 5.2 is modelled using the apparent log K$_{sp}$ for RaSO$_4$ using parameters that were obtained in a regression (see Appendix I). As can be observed, the fit is acceptable. The obtained values for the NaSO$_4^-$ ion pair stability constants are also in agreement with the trend observed by other research for this ion pair [BUC99, DAL72]. Extrapolation gives the value of logarithm of RaSO$_4$ solubility product constant at zero ionic strengths at 25 ºC of - 10.16 ± 0.05. This value is within the experimental uncertainty of the value proposed by Brown and co-workers (-10.21) [BRO15].

The solubility of BaSO$_4$ has been studied by many researchers in different media, temperatures and pressures. A detailed review of the data was presented by Monnin [MON88, MON99]. He found that the experimental data of Templeton [TEM60] for BaSO$_4$ solubility, also in NaCl media and at 25.1 ºC, is in good agreement with the data from other researchers and therefore can be considered as reliable. The obtained apparent log K$_{sp}$ for RaSO$_4$ can be compared with apparent log K$_{sp}$ for BaSO$_4$ taken from Templeton [TEM60] (Fig. 5.2).

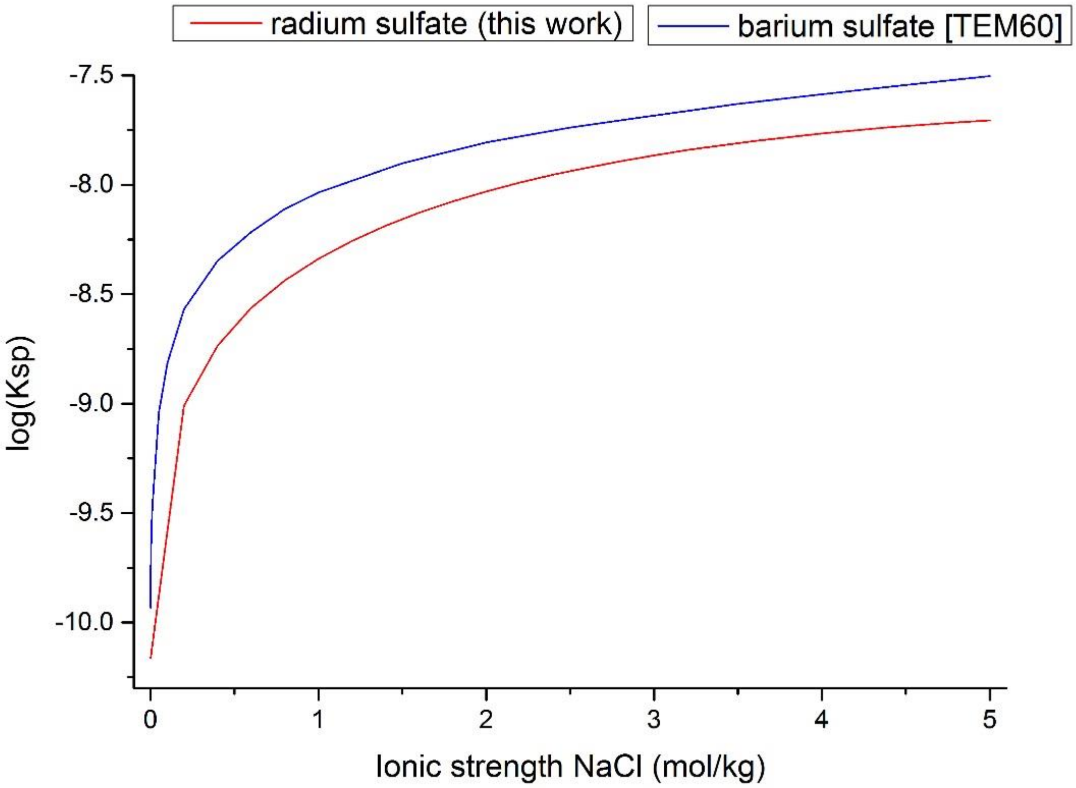

Figure 5.3 Comparison of logarithm of apparent $RaSO_4$ and $BaSO_4$ solubility product constants at different ionic strengths in NaCl media at 25ºC

As can be observed from Fig. 5.3, the solubilities of $BaSO_4$ and $RaSO_4$ follow the same trend, which indicates the similarity of ion interaction parameters of Ba^{2+} and Ra^{2+}.

The plot of logarithm of solubility product constants of strontium, barium (both taken from [FEL90]) and radium sulfate at zero ionic strengths and 25.1 ºC against reciprocal of the effective ionic radii of these elements in 8-fold coordination is shown in Fig. 5.4.

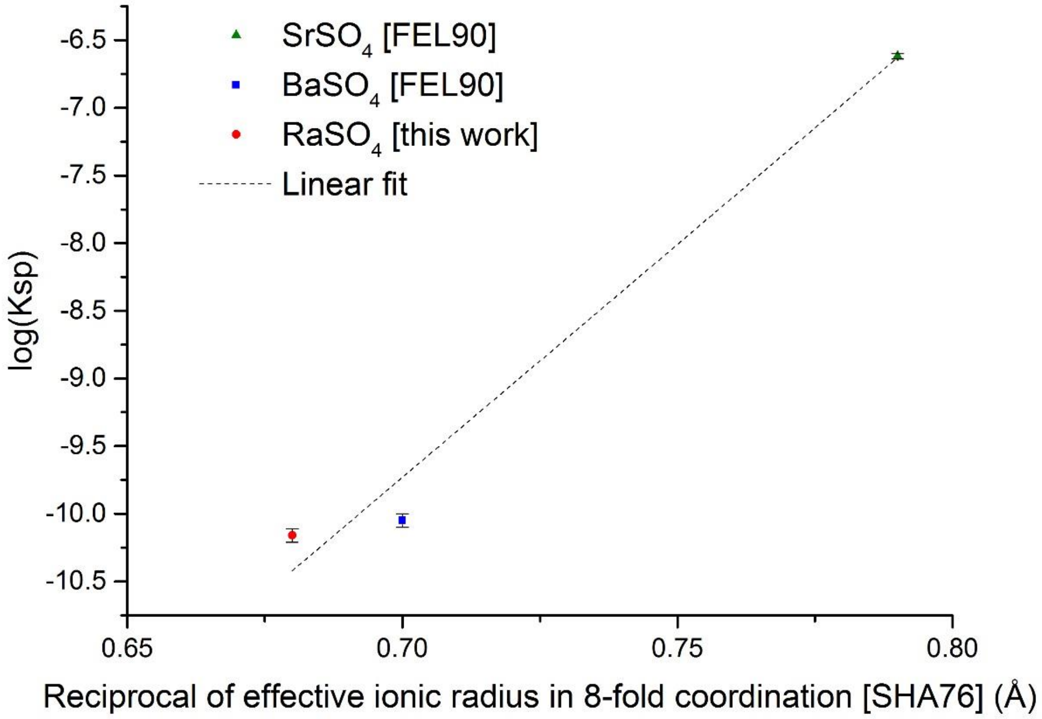

Figure 5.4 Comparison of $RaSO_4$, $BaSO_4$ and $SrSO_4$ solubility product constants at zero ionic strength using reciprocal of the effective ionic radii of these elements

As can be observed from Fig. 5.4 the fit is good and such extrapolation could be used to get first estimate of alkaline-earth sulfate solubilities [BRO15].

5.3 Solubility of radium carbonate

Analysis of the experimental data of $RaCO_3$ solubilities was almost the same as the analysis for $RaSO_4$ data described above and in Appendix I. The only difference was that at such high pH (>13) the hydrolysis of radium has to be taken into account. The results are listed in Table 5.3.

Extrapolation of $[Ra^{2+}]^{free}$ to zero ionic strength as was done in the case of sulfate system is shown in Fig.5.5 The results of $RaCO_3$ solubility determinations are listed in Table 5.3. Extrapolation to zero ionic strength is shown in Fig.5.6.

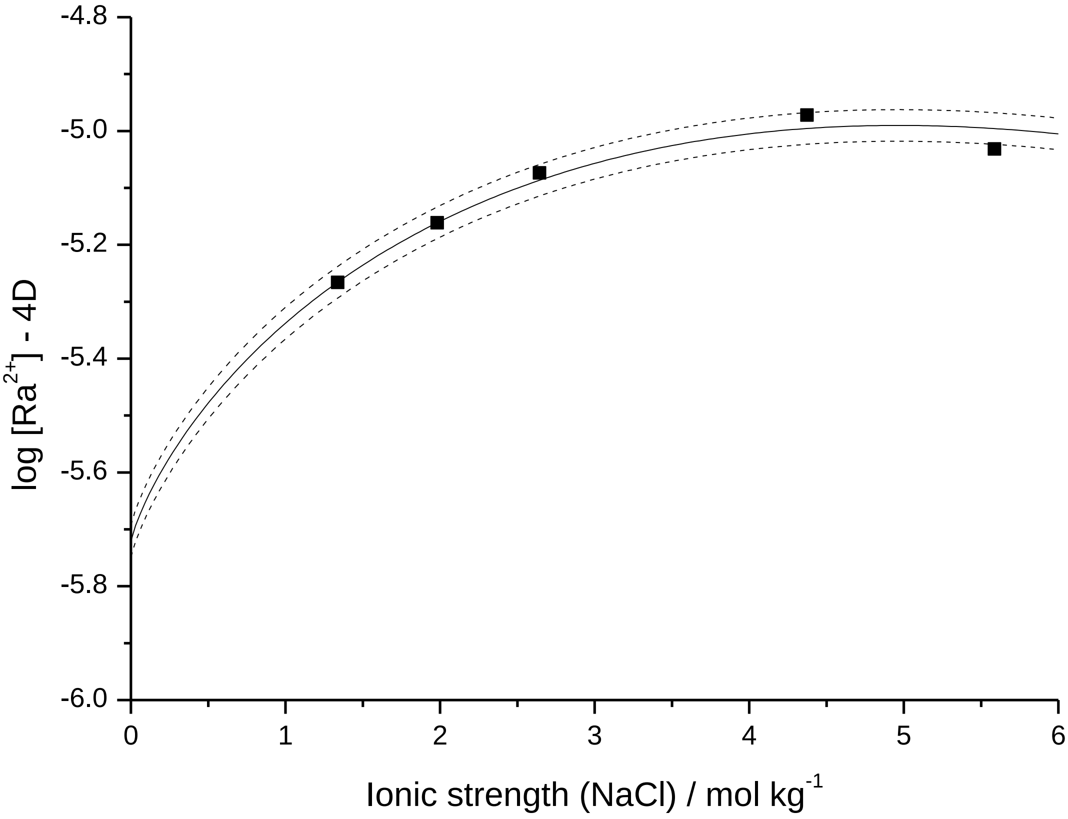

Figure 5.5 Extrapolation of log$[Ra^{2+}]^{free}$ to zero ionic strength using extended Specific ion Interaction Theory (equation A10 in Appendix I). The ion interaction parameters were fixed and taken from sulfate system; log$[Ra^{2+}]^0 = -5.72\pm0.03$, $\varepsilon_1(Ra^{2+}\text{-}Cl^-) = -0.38$ - fixed, $\varepsilon_2(Ra^{2+}\text{-}Cl^-) = 0.34$ – fixed. The dotted lines are the 2-sigma (95 % confidence) lines.

Table 5.3 Results of radium carbonate solubility determination at 25.1°C

Ionic strengths NaCl, mol·kg^{-1}	**$[Ra]^{total}$, M**	**Apparent logK$_{sp}$**
1.34	$(1.19 \pm 0.06)\cdot10^{-4}$	-5.90 ± 0.11
1.98	$(1.22 \pm 0.06)\cdot10^{-4}$	-5.78 ± 0.07
2.64	$(1.15 \pm 0.06)\cdot10^{-4}$	-5.67 ± 0.08
4.37	$(1.22 \pm 0.06)\cdot10^{-4}$	-5.44 ± 0.08
5.58	$(1.13 \pm 0.06)\cdot10^{-4}$	-5.39 ± 0.11

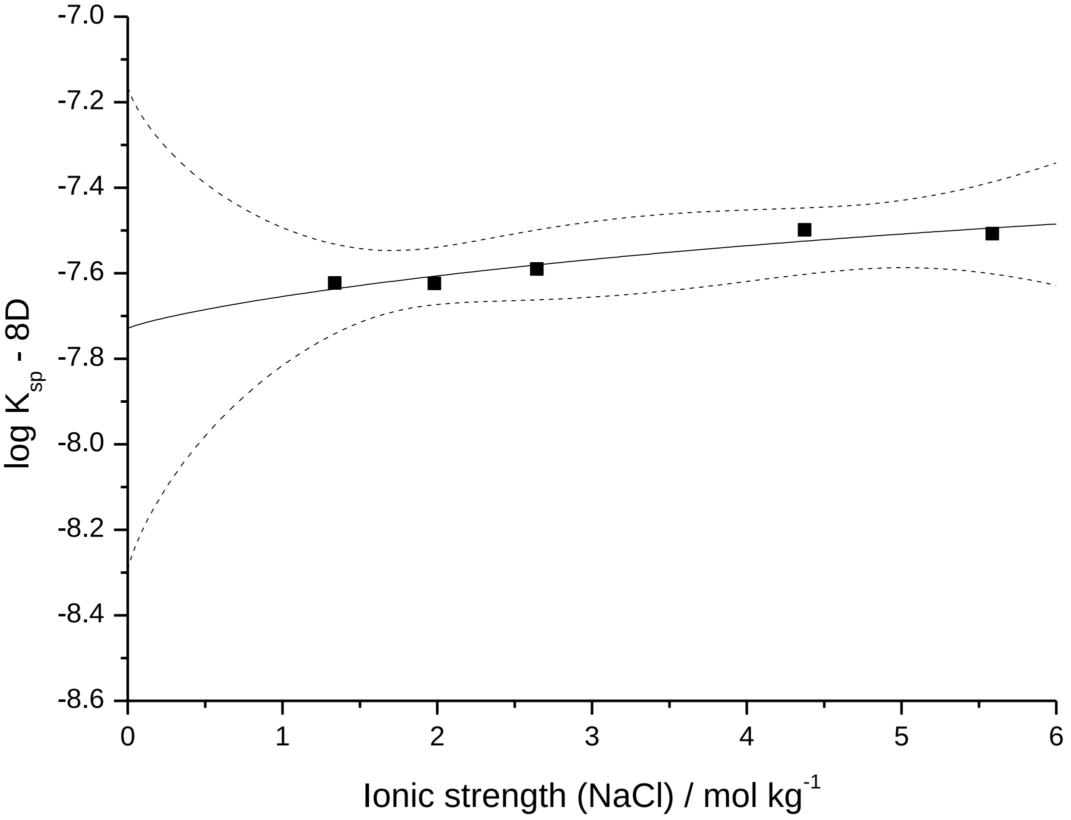

Figure 5.5 Extrapolation of logK_{sp} of $RaCO_3$ to zero ionic strength using extended Specific ion Interaction Theory (equation A17 in Appendix I). The following parameters were obtained in a regression; logK_{sp}^0 = -7.73±0.56, ε_1(sp) = -0.07±0.42, ε_2(sp) = 0.04±0.43. The dotted lines are the 2-sigma (95 % confidence) lines.

The solid curve in Fig. 5.5 is the modelled apparent log K_{sp} for $RaCO_3$ using parameters that were obtained in the regression. As in the case of $RaSO_4$, the fit is acceptable and the change in obtained values for the $NaCO_3^-$ ion pair stability constants with the change of ionic strength is expected. Moreover, the obtained stability constant for $NaCO_3^-$ is higher than the stability constant obtained for $NaSO_4^-$, which was also expected. The value of -7.73 ± 0.56 for the logarithm of $RaCO_3$ solubility product constant at zero ionic strengths at 25 ºC was obtained. The high uncertainty for the $RaCO_3$ solubility at zero ionic strength can be explained by the lack of experimental data at ionic strengths lower than 1 M.

The solubility of $BaCO_3$ in NaCl media and at 25.1 ºC had been studied by Millero and co-workers, among others [MIL84]. A comparison of the $RaCO_3$ solubility model with the model of $BaCO_3$ obtained by Millero and co-workers [MIL84] can be seen in Fig. 5.5.

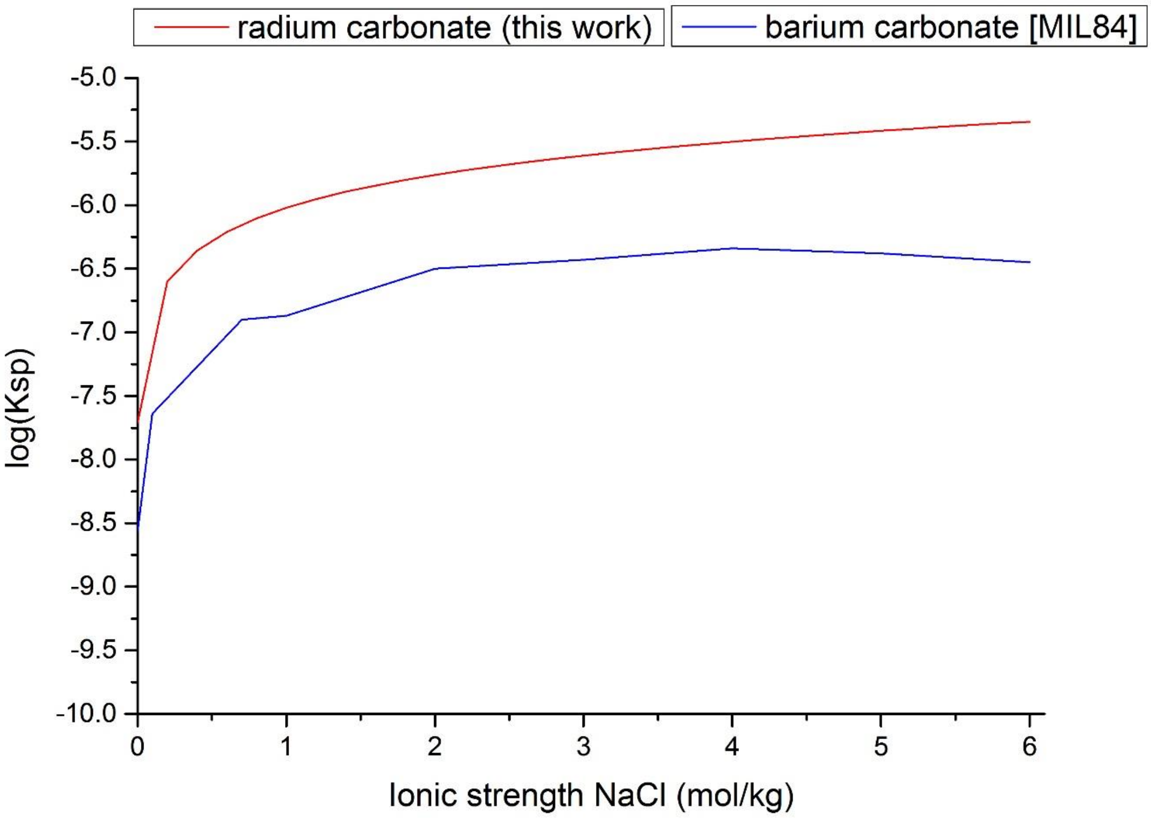

Figure 5.6 Comparison of logarithm of apparent $RaCO_3$ and $BaCO_3$ solubility product constants at different ionic strengths in NaCl media at 25 °C

As in the case of $RaSO_4$ and $BaSO_4$ the solubilities of $RaCO_3$ and $BaCO_3$ follow the same trend as expected because experiments were done in the same medium (NaCl). As discussed in the theoretical part of this work, according to the present theoretical model developed by Debye and Hückel [DEB23] a change of the solubility at a particular ionic strength from the solubility at the hypothetical zero ionic strength is attributed to short- and long-range electrostatic interactions (or activity coefficients). On the one hand it can be argued that because of the similarity of the effective ionic radii of Ba^{2+} (1.42 Å in 8-fold coordination [SHA76]) and Ra^{2+} (1.48 Å in 8-fold coordination [SHA76]) and the same charge both ions undergo similar short- and long-range electrostatic interactions in NaCl media as shown in Fig. 5.3 and Fig. 5.6 (or activity coefficients of Ra^{2+} and Ba^{2+} are close to each other). It leads to the conclusion that these electrostatic ion interactions or activity coefficients depend on the effective ionic radius. On the other hand this assumption is not valid for other metal ions with similar effective ionic radii. Therefore, it can be concluded that all the approaches for activity coefficient modelling are semi-empirical, with one or more fitting parameters, and probably there is no fundamental understanding of this phenomenon. The assumption that these forces are of an electrostatic nature at ionic strengths higher than 0.1 M can be always brought into question.

The log K_{sp} plot for strontium, barium (taken from [MIL84]) and radium carbonates at zero ionic strength and 25.1 °C against reciprocal of the effective ionic radii of these elements in 8-fold coordination is shown in Fig. 5.7.

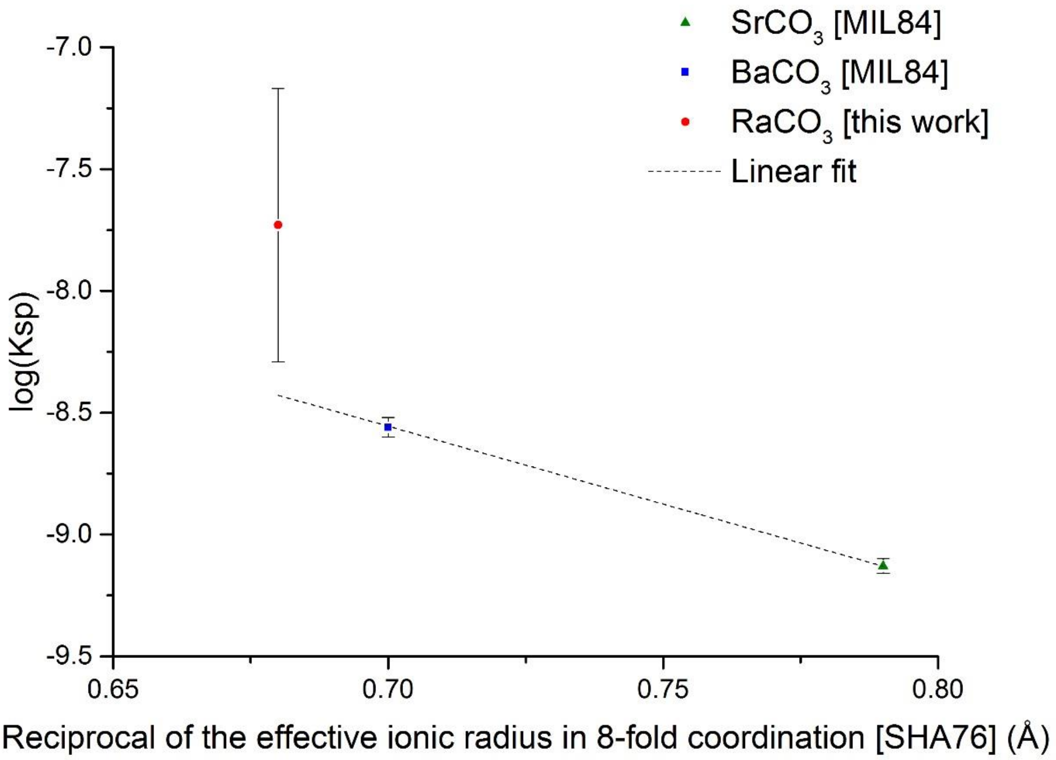

Figure 5.7 Comparison of $RaCO_3$, $BaCO_3$ and $SrCO_3$ solubility product constants at zero ionic strength using reciprocal of the effective ionic radii of these elements

As can be observed from Fig 5.7 the fit for alkaline-earth carbonates is poor, which can be compared with the case of alkaline-earth sulfates in Fig. 5.4. Langmuir and Riese used such a model to estimate the log K_{sp} value of $RaCO_3$ at zero ionic strength at 25.1 ºC and obtained a value of -8.3, which differs from the value obtained in this work (-7.73) even taking into account the high uncertainty. However, in 1937 Nikitin wrote, “Thus we see that the weight solubilities of radium and barium carbonates differ approximately 10 times at this [experimental] conditions” [NIK37]. Taking into account that Nikitin added NH_4Cl as a background electrolyte, NaOH to increase the pH and $(NH_4)_2CO_3$ it can be concluded that the value obtained in this work is in excellent agreement with the assumption that Nikitin made a long time ago, based on his experimental result. Almost identical activity coefficient changes for Ba^{2+} and Ra^{2+} as illustrated in Fig. 5.6 shows that Nikitin produced high quality data in 1937, even probably without detailed knowledge of activity coefficient phenomena (at that time only the Debye-Hückel limiting law was well-established and calculation of activity coefficients at such high ionic strengths at which Nikitin worked was not possible).

Fig. 5.7 shows that extrapolation of solubility product constants of alkaline-earth metals carbonates using only the electrostatic model is doubtful and probably some other phenomena influence solubility at zero ionic strength.

6. Conclusion

In this work an old radium source previously used in radiation therapy was safely disassembled using modern radiation protection standards. The outer steel plaques were dissolved in concentrated HCl at elevated temperature, and the platinum-gold cylinders were cut mechanically. $RaSO_4$ was converted into $RaCO_3$ using the Curie method, which includes several cycles of $RaSO_4$ boiling in concentrated Na_2CO_3 solutions. The structural property of the prepared $RaCO_3$ precipitate was characterized by XRD and it was found that these particular conditions lead to the formation of amorphous $RaCO_3$. A subsequent heat treatment step has to be performed to crystallize the $RaCO_3$. Another part of $RaCO_3$ was dissolved in HCl and a 0.40 ± 0.02 mM radium solution was obtained. The purity of the solution was verified using HPGe measurements, which confirmed that the procedure allowed radium to be separated from its decay products and thus a high purity radium solution was obtained.

It can be concluded that the method of $RaSO_4$ dissolution using chelating agents, for example Na_2EDTA, allows for a conversion of more than 90 % of the radium into the aqueous solution at room temperature in 30 minutes, but leads to problems in radium stripping or separation. The method based on reduction of $Ra(Ba)SO_4$ using $NaNO_2$ at room temperature requires addition of concentrated acids. The ion exchange method is a promising method for $RaSO_4$ dissolution, but further detailed studies are required to find optimal conditions. For these reasons the conversion of $RaSO_4$ into aqueous solution using $RaCO_3$ precipitation at elevated temperatures, sometimes referred to as the Curie method, can be considered to be the most appropriate method for obtaining high purity dilute radium solutions, since this method does not require high temperature, oxygen-free atmosphere, special equipment or additional separation steps.

It was shown that the solubilities of alkaline-earth carbonates cannot be predicted by extrapolation from the same alkaline-earth compound solubilities using effective ionic radii with the same coordination number. It was demonstrated that the shapes of radium sulfate and carbonate solubility curves are almost identical to the shapes of the corresponding barium solubility curves, which may indicate that radium undergoes similar specific ion interactions as barium in NaCl media.

7. Future work

The solubility of $RaCO_3$ will be studied from undersaturation. XRD pattern of $RaCO_3$ and $RaSO_4$ will be obtained. It would be interesting to study radium hydrolysis and complex formation of $RaSO_4(aq)$ and $RaCO_3(aq)$ but there are both experimental and theoretical difficulties. It would also be interesting to determine ion interaction parameters of Ra^{2+} with some other inorganic ligands and compare these with other alkaline-earth metals. Phosphate is omnipresent ligand in the environment and therefore experimental determination of radium phosphate solubility would seem warranted.

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Appendix I

Adaptation of the Extended Specific Ion interaction theory

The extended specific ion theory will be adapted for the particular $RaSO_4$ solubility case to derive hybrid extended specific ion theory. As previously mentioned, it can be supposed that NaCl is a strong electrolyte and is completely dissociated in aqueous solutions in this particular case. It is also supposed that alkaline-earth metals form weak complexes with sulfate ions. Thus, the total concentration of radium in the aqueous phase that was measured is equal to:

$$[Ra]^{total} = [Ra^{2+}]^{free}_{apparent} + [RaSO_4^{aq}] \qquad \text{A1}$$

Two equilibria occur:

$$Ra^{2+} + SO_4^{2-} \rightarrow RaSO_4^{aq}$$

$$RaSO_4^{solid} \rightarrow Ra^{2+} + SO_4^{2-}$$

Equilibrium constants for these reactions are:

$$K^0_{IP} = \frac{[RaSO_4^{aq}] \cdot \gamma_{\mathrm{RaSO_4^{aq}}}}{[Ra^{2+}]^{free} \cdot \gamma_{Ra^{2+}} \cdot [SO_4^{2-}]^{free} \cdot \gamma_{SO_4^{2-}}} \qquad \text{A2}$$

$$K^0_{SP} = [Ra^{2+}]^{free} \cdot \gamma_{Ra^{2+}} \cdot [SO_4^{2-}]^{free} \cdot \gamma_{SO_4^{2-}} \qquad \text{A3}$$

The concentration of $RaSO_4^{aq}$ ion pairs can be derived from equation A2 assuming that the activity coefficient for $RaSO_4^{aq}$ is close to unity and can be neglected:

$$[RaSO_4^{aq}] = K^0_{IP} \cdot [Ra^{2+}]^{free} \cdot \gamma_{Ra^{2+}} \cdot [SO_4^{2-}]^{free} \cdot \gamma_{SO_4^{2-}} \qquad \text{A4}$$

Equations A3 and A4 can be combined:

$$[RaSO_4^{aq}] = K^0_{IP} \cdot K^0_{SP} \qquad \text{A5}$$

As can be observed from equation A5, the concentration of $RaSO_4^{aq}$ ion pairs will be constant at all ionic strengths. Insertion of A5 into A1 and addition of the activity coefficient gives:

$$[Ra]^{total} = \frac{[Ra^{2+}]_0^{free}}{\gamma_{Ra^{2+}}} + K_{IP}^0 \cdot K_{SP}^0 \qquad \text{A6}$$

Rearrangement and taking the logarithms gives:

$$\left([Ra]^{total} - K_{IP}^0 \cdot K_{SP}^0\right) \cdot \gamma_{Ra^{2+}} = [Ra^{2+}]_0^{free} \qquad \text{A7}$$

$$\log\left([Ra]^{total} - K_{IP}^0 \cdot K_{SP}^0\right) + \log(\gamma_{Ra^{2+}}) = \log([Ra^{2+}]_0^{free}) \qquad \text{A8}$$

The extended Specific Ion Interaction Theory (extended SIT) states:

$$\log(\gamma_i) = \frac{-z_i^2 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + (\varepsilon_1 + \varepsilon_2 \log(I)) \cdot I \qquad \text{A9}$$

The activity coefficient of Ra^{2+} can be derived from the extended SIT and inserted into equation A8:

$$\log\left([Ra]^{total} - K_{IP}^0 \cdot K_{SP}^0\right) - \frac{z_i^2 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} = \log([Ra^{2+}]_0^{free}) - (\varepsilon_1^{Ra} + \varepsilon_2^{Ra} \log(I)) \cdot I \qquad \text{A10}$$

As previously shown Na^+ forms ion pairs with SO_4^{2-} and the total concentration of SO_4^{2-} in the aqueous phase that was measured is equal to:

$$[SO_4]^{total} = [SO_4^{2-}]^{free} + [NaSO_4^-] \qquad \text{A11}$$

Sodium and sulfate form an ion pair according to the reaction:

$$Na^+ + SO_4^{2-} \rightarrow NaSO_4^-$$

Equilibrium constants for this reaction are:

$$K_{IP(NaSO_4^-)}^0 = \frac{[NaSO_4^-] \cdot \gamma_{\mathrm{NaSO_4^-}}}{[Na^+]^{free} \cdot \gamma_{Na^+} \cdot [SO_4^{2-}]^{free} \cdot \gamma_{SO_4^{2-}}} = K_{IP(NaSO_4^-)}^{apparent} \cdot \frac{\gamma_{\mathrm{NaSO_4^-}}}{\gamma_{Na^+} \cdot \gamma_{SO_4^{2-}}} \qquad \text{A12}$$

Concentration of $NaSO_4^-$ can be derived from equation A12:

$$[NaSO_4^-] = K^{apparent}_{IP(NaSO_4^-)} \cdot [Na^+]^{free} \cdot [SO_4^{2-}]^{free} \qquad \text{A13}$$

Equation A13 can be inserted into equation A11:

$$[SO_4]^{total} = [SO_4^{2-}]^{free} + K^{apparent}_{IP(NaSO_4^-)} \cdot [Na^+]^{free} \cdot [SO_4^{2-}]^{free} \qquad \text{A14}$$

$$[SO_4]^{total} = [SO_4^{2-}]^{free} \cdot (1 + K^{apparent}_{IP(NaSO_4^-)} \cdot [Na^+]^{free}) \qquad \text{A15}$$

Rearrangement gives:

$$[SO_4^{2-}]^{free} = \frac{[SO_4]^{total}}{1 + K^{apparent}_{IP(NaSO_4^-)} \cdot [Na^+]^{free}} \qquad \text{A16}$$

The stability constant for the sodium sulfate ion pair in logarithmic form with activity coefficients derived from extended specific ion interaction theory:

$$\log\left(K^{apparent}_{IP(NaSO_4^-)}\right) - \frac{z_i^2 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} = \log\left(K^0_{IP(NaSO_4^-)}\right) - (\varepsilon_1^{Na} + \varepsilon_2^{Na} \log(I)) \cdot I \qquad \text{A16}$$

Finally, the $RaSO_4$ solubility constant A3 in logarithmic form with activity coefficients derived from extended specific ion interaction theory can be obtained:

$$\log\left(K^{apparent}_{SP}\right) - \frac{z_i^2 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} = \log\left(K^0_{SP}\right) - (\varepsilon_1^{RaSP} + \varepsilon_2^{RaSP} \log(I)) \cdot I \qquad \text{A17}$$

Thus, the following parameters can be obtained in a regression to minimize errors:

$$\log\left(K^0_{SP}\right),\ \varepsilon_1^{RaSP},\ \varepsilon_2^{RaSP}, \log\left(K^0_{IP(NaSO_4^-)}\right),\ \varepsilon_1^{Na}, \varepsilon_1^{Na} \qquad \text{A18}$$